THE PREPARATION AND COMPLEXING PROPERTIES OF ISOCYANIDE-FUNCTIONALIZED POLYMERS.

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by

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ABSTRACT

This thesis is concerned with the synthesis of an isocyanide-functionalized polymer support and an investigation of the metal complexing properties of the resin produced.

The synthesis of two functionalized monomers, p-vinylbenzylformamide and m/p-vinylbenzylphthalimide is described. Each of these monomers was in turn copolymerized in water suspension with styrene and divinylbenzene, in an attempt to synthesize suitably functionalized highly crosslinked macroporous resins. The production of low crosslinked microporous (or gel-type) resins by the suspension copolymerization of the phthalimide monomer with styrene and divinylbenzene is also described. These microporous resins were then further chemically modified to yield the polymer-supported isocyanide.

The metal complexing properties of the polymer-supported isocyanide were studied. It was shown to extract a variety of normal oxidation state metals from aqueous tetrahydrofuran and anhydrous metal salts and organometallic complexes from tetrahydrofuran or toluene. The structures of the complexed species are assigned on the basis of elemental analyses and infrared spectra.

Acknowledgments.

Abstract.

CHAPTER ONE: INTRODUCTION

The immobilization of soluble metal complexes on suitably functionalized organic or inorganic supports offers potential advantages in catalysis, where rates and selectivity for reactions may be enhanced, and may also be useful in metal separation, for example in affinity chromatography, and in metal extraction and recovery, where the functional group shows some selectivity in reversibly binding the metal complexes. The advantage of employing polymer supports lies in their insolubility in either organic or inorganic media, so that separation from the reaction mixture requires only simple filtration. Many different functionalities have been generated on simple styrene-divinylbenzene polymers to carry out these different separations; for example, a considerable volume of work on polymer-supported catalysts has been carried out on polystyrene supports having phosphine as the functional group. Only recently has a small amount of work been reported on the use of isocyanide-functionalized polymers - a potentially very useful class of functionalized resins. The isocyanide ligand (R - N ≡ C) is one of the most versatile available to the transition metal chemist, forming a variety of complexes with both medium oxidation state metals and metals in low oxidation states.

This thesis is concerned with the preparation of isocyanide-functionalized polystyrene resins and an investigation of their complexing properties. After a general introduction (Chapter 1), the synthesis of the functionalized monomers, and their subsequent polymerization and further modification is described (Chapter 2), while Chapter 3 deals with the complexation for various metal complexes and metal salts by these functionalized polymers.

1. Polymer Supports

1.1. General Introduction to polymer supports

Polymer Chemistry has, until recently, centred on the synthesis and evaluation of physical properties of new material. However the use of polymer supports has become an area of extensive interest since the pioneering work of Merrifield in 1963[1]. The term "supported" describes the case of a structurally well-defined molecule which is attached by covalent or ionic bonds to an organic polymeric or inorganic oxide backbone. The term "immobilized" is more frequently used, in place of "supported", for polymer supports of biological importance. In polymer-supported reactions, the term "resin" is usually used to describe polymers which are crosslinked and are therefore, insoluble. The most common form of shorthand notation used to indicate a polymer support is shown below:

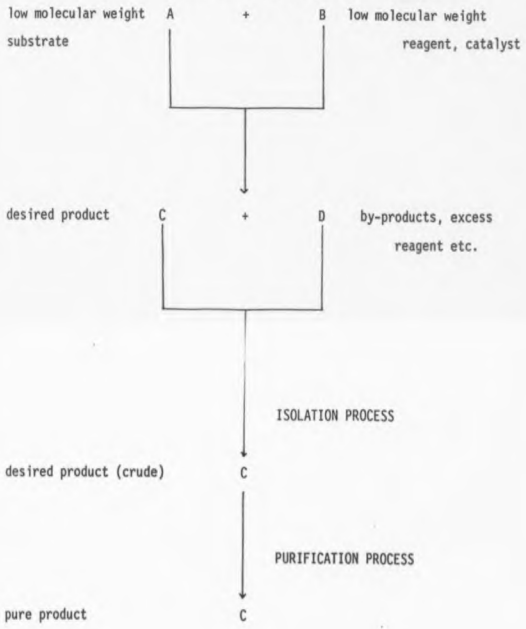
this implies an organic macromolecular or polymeric support with the most important pendant group displayed. The use of the symbol

implies a support which may be inorganic or organic. Any further information about the nature of the support will be detailed in the text.

Polymer supports can be used in a variety of different ways, and this is illustrated with reference to the scheme shown in figure 1 for a

conventional organic synthesis. Here the substrate is treated with a reagent, reagents or a catalyst of some kind during which the substrate is converted (partially or completely) into the product. The product (C in fig.1) must then be isolated from the reaction mixture. This separation is achieved by conventional procedures such as crystallization, distillation, sublimation, and various chromatographic techniques.

Fig.1. Scheme for a conventional organic synthesis



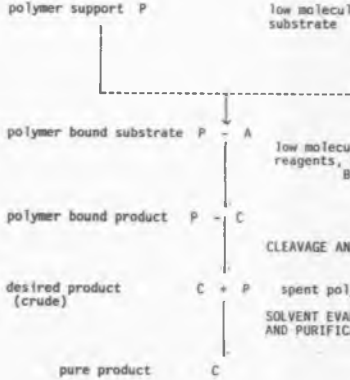


Fig.2. Scheme for synthesis using polymer-supported substrates.

* may be re-usable

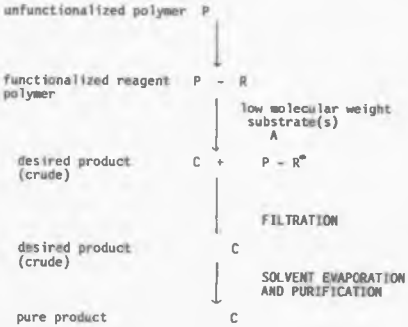


Fig.3. Scheme for synthesis using polymer-supported catalysts.

*should be re-usable

The isolation process often involves more than one of the above operations to obtain the pure product (C). The isolation step is frequently the more time-consuming part of the synthesis. By using polymers to support one of the reactant species, the work-up procedure for the isolation of the product can be very much simplified, since crosslinked supports are insoluble and may be removed from the reaction mixture by filtration. (Figs. 2 and 3).

The polymer support can be used in several ways:

(i) as a support for a catalyst[2,3] or a biological enzyme

(ii) as a support for a reagent[4 - 6], either transferring a functional group to a soluble substrate, or modifying the latter.

(iii) The polymer may act as a support and also as a protecting group since the site of attachment is reversibly blocked on the substrate molecule. Therefore these groups cannot participate in the reaction. For example polymer supports have been used as monoblocking groups in effecting a chemical reaction at one end only of a completely symmetrical long chain diacid chloride.[7] The unattached end can then undergo further reactions before cleavage from the support. In the example quoted the only products isolated were monomethyl ester monoamides in high yields (around 90%). No diesters (resulting from unreacted starting material) or diacid chloride doubly-bound (i.e. both ends) to the polymer were detected.

(iv) The polymer support may be used to selectively extract a compound from the reaction mixture, by reversibly binding to one of the components. (This may of course be used to extract either the desired or undesired products as appropriate). Examples are metal ion extraction and separations by affinity chromatography[8,9].

The main advantages of polymer supports over their non-supported analogues are:-

(i) Ease of recovery/work-up procedure; the polymeric reagent or catalyst can be removed from the reaction mixture by filtration, decantation or centrifugation.

(ii) Reaction yields may be improved; large excesses of reagents can be used to enhance the rate of diffusion to a reactive site or saturate the system and thus push the reaction to completion, without causing separation problems.

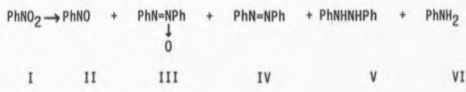
(iii) If the polymeric reagent can be easily regenerated by a single reaction after use, and the reactions in which it is involved proceed virtually to completion, it may be possible to automate the process. This is obviously beneficial in industrial processes.

(iv) The ability to recover and re-use the polymeric species is particularly important in the case of supported precious metal catalysts, as these are often expensive.

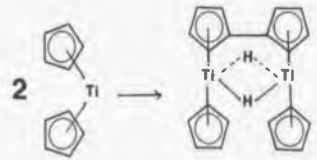
(v) Multistep syntheses can be simplified by having each of the successive products bound to the polymer. This approach is often used in the synthesis of peptides, oligo- and polynucleotides and oligosaccharides. For example, in the original Merrifield synthesis a protected amino acid is bound to a substituted chloromethyl polystyrene[1]. The protecting group is then removed and a second (protected) amino-acid is attached to the first. This process is repeated until the required unit is attached to the polymer, then a cleavage reaction is performed.

Sequential cyclooligomerization of butadiene, followed by hydrogenation of the products was carried out by Pittman and Smith[10], using a phosphinated polystyrene resin to which $(PPh_3)_2Ni(CO)_2$ and $(PPh_3)_3RhCl$ had been anchored. The two catalysts did not interfere with each other and could be recovered and recycled.

(vi) The physical presence of the polymer may exercise thermodynamic or kinetic control of substrates attempting to gain access to the reactive sites in the polymer matrix, giving rise to a different product distribution relative to the homogeneous reaction. For example, in the reduction of certain aromatic nitro derivatives by sodium borohydride, using either a supported or homogeneous nickel catalyst, it was found that in the supported reactions a greater proportion of III was found, a small quantity of IV and no VI, relative to a distribution of 10% III, 40% IV and 40% VI in the homogeneous reactions.



(vii) The use of a polymer support may help to promote intra- rather than inter-molecular reaction and also to prevent dimerization. The reactive molecules can be "diluted" by anchoring them at distances far enough apart to prevent inter-molecular reaction. In these instances a highly crosslinked resin is often used to provide a rigid matrix. For example, polymer supports have been used to anchor the highly reactive titanocene molecule.[11,12] Titanocene is a catalyst in the hydrogenation of various unsaturated organic compounds and molecular nitrogen, but its efficiency is considerably reduced because of its tendency to dimerize.



The titanocene precursor was anchored on a 20% crosslinked polymer support, and on reduction produced a catalyst whose hydrogenation efficiency was greater (factor 25 - 120) than the non-attached species.

(viii) The polymer support often confers increased stability on air or water sensitive reagents. For example, Pittman et al [13] state that the supported hydroformylation catalyst "could be repeatedly recycled and even exposed to water without drastic loss of activity".

(ix) Crosslinked polymers are insoluble, non-volatile and therefore non-toxic and odourless. The supported reagent is also, therefore, rendered non-toxic and odourless. This is a particularly beneficial property in the present case since liquid (monomeric) isocyanides of low molecular weight have very disagreeable odours and some toxicity.

As with any synthetic method, the use of polymer supports has several disadvantages also[14], which can summarised as follows:

(i) The synthesis will have the additional steps of attachment to and cleavage from the polymer, (attachment only for catalysts). This may lead to a decrease in yield of product.

(ii) Lower yields may also be caused by polymer-generated steric hindrance of reactants (the pore size may be too small, and so hamper diffusion to the reactive site); also the polymer support may not be compatible with certain types of reagents. Thus polystyrene, being non-polar (and hydrophobic) is incompatible with highly polar molecules, i.e. they are not able to diffuse into the active sites on the support.

(iii) Difficulty is experienced in monitoring reactions since the polymers are insoluble, therefore making reactions almost impossible to follow using either ultraviolet spectroscopy or nuclear magnetic resonance spectroscopy techniques. Thus, only infra-red spectroscopy and elemental analyses are commonly available for the determination of the structure of the supported species.

(iv) Since reactions rarely go to 100% yield, there will be some residual functionality from each stage in the synthesis. These may interfere with the uses of the final product. Also, a considerable number of experiments may be necessary to determine the optimum conditions for the supported reaction, as these conditions may be quite different from those for the non-supported reaction.

(v) There may be changes in the mechanism of the reaction when polymeric rather than low molecular weight reagents are used. This is found to be the case in brominations using poly-N-bromosuccinimide[15], where products were formed which resulted from bromination other than from the usual benzylic bromination observed with the unsupported species. Thus the new product distribution pattern may result in poor yields of the desired product.

(vi) If the polymer-supported reagent or catalyst is not regenerable, it is generally more expensive to produce than the non-supported analogue. If the reagent is regenerable, the degree of functionalization may be reduced during the regeneration process. This was observed in the synthesis of a supported carbodiimide, where the activity of the recovered polymeric species was generally less than the starting material[16]. In the synthesis of a polymer-supported organotin dihydride reagent, Weinshenker, Crosby and Wong[17] found only 60% of the activity of the supported reagent could be regenerated from unused resin after storage.

Problems may also arise from reduced activity and leaching of metal[18] from polymer-supported catalysts.

1.2. Organic Supports

1.2.1. Suspension Polymerization

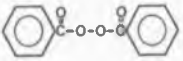
Although several types of organic material have been used as polymer supports, the most commonly employed system uses styrene/divinylbenzene based resins, produced by suspension copolymerization. By this method, the monomers are broken down into spherical droplets and dispersed (by mechanical stirring) in an immiscible liquid, usually water. The suspension is maintained by stirring and the use of suspension stabilizers, for example poly(vinyl alcohol), [88% hydrolysed from poly(vinyl acetate)]. Although the quantities of reagents used varies considerably, the monomer:water ratio is generally about 1:10, and the weight ratio of stabilizer to monomer is in the range 1:20 to 1:7. Stabilizers with an average molecular weight in the range 25,000 - 100,000 are effective and convenient to use experimentally.

The organic phase therefore contains:

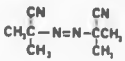
(a) the monomers - styrene, divinylbenzene and possibly another functionalized styrene monomer;

(b) a diluent, or diluent system (if used) - see later;

(c) a free radical initiator - benzoyl peroxide (1) or azobisisobutyronitrile (2).



(1)



(2)

The suspension stabilizer is dissolved in the aqueous phase. The polymerization mixture is stirred (usually at speeds of about 800 rev min^{-1} in a specially designed baffled reactor. The shape of the reactor and of the stirrer are designed such that an optimum flow pattern for maintaining suspension is achieved. One of the problems experienced in such polymerizations is the aggregation of the polymerizing droplets. The design of the reactor and stirrer is critical in producing an optimum flow pattern for maintaining an efficient suspension. Thus the rate of agitation may be minimized, therefore reducing the energy of particle collisions and preventing agglomeration.

The polymerization mixture is heated to temperatures of about 60 - 80°C, (dependent upon the initiator used) which will produce thermal fragmentation of the initiator and thus the polymerization proceeds. After several hours, when the polymerization is complete, (the spherical liquid monomer droplets having been converted into spherical solid polymer particles, or beads,) the product can be collected by filtration, and washed free of stabilizer and other contaminants.

The particle size of the product is influenced by a number of factors, but the most important are

(a) organic phase to water ratio
(b) rate of agitation
(c) geometry of the reaction vessel
(d) nature of the suspension stabilizers

These factors are illustrated in the semi-quantitative equation below[19].

$$d \propto \frac{K.\sigma.\phi}{L,N,P}$$

d = particle size
K = shape Factor
σ = interfacial tension between liquid phases
ϕ = volume fraction of the dispersed phase
P = droplet density
L = stirrer diameter
N = stirrer speed

Normal suspension techniques produce average particle diameters commonly in the range 300 - 100 μm.

In almost all of the styrene/divinylbenzene copolymer resins, commercial divinylbenzene is used. This is usually a complex mixture which contains, on average, about 55% actual divinylbenzene.

A typical sample[20] contains 35% m-divinylbenzene
16% p-divinylbenzene
31% m-ethylstyrene
15% p-ethylstyrene
3% diethylbenzenes

Hence the nominal crosslink ratio is often quoted as being (approximately) equal to half the percentage of commercial divinylbenzene used.

However, in the subsequent work described in this thesis, a figure of 63% actual divinylbenzene was determined for the commercial divinylbenzene supplied, and this is used in all calculations.

The rate at which these monomers are incorporated into the growing polymer chains varies when styrene and commercial divinylbenzene are copolymerized. Styrene and the ethylstyrenes have a similar reactivity[21], (see fig.4), but the first double bond in the divinylbenzenes has been shown to be more reactive than styrene, the para isomer being the most reactive[22-24]. The remaining double bond in the divinylbenzene has a reactivity similar to that of styrene[25]. As a result of the somewhat higher reactivity of divinylbenzene, its isomers will be incorporated into the growing chains at a faster rate than styrene or the ethylstyrene isomers.

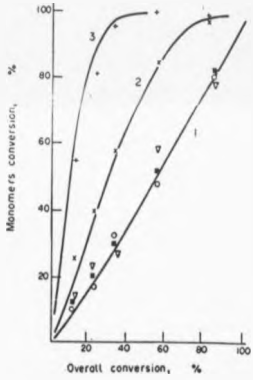


Fig.4. Calculated curves for conversion of :

1 Styrene and ethylvinylbenzene

2 m.DVB

3 p.DVB

Experimental points

Styrene o

p.Ethylvinylbenzene ▽

m.Ethylvinylbenzene ■

p.DVB +

m.DVB x

In a suspension copolymerization, each droplet of the organic phase behaves as an individual bulk polymerization that results in a copolymer bead.

Each droplet is composed of the monomers, initiator and diluent (if used), suspended in aqueous solution. Initiation occurs evenly throughout the droplets, and the polymer chains grow by addition of monomer units, and is initially composed of straight chains. When a divinylbenzene unit is incorporated into a chain a pendant double bond is present which can then be incorporated in another growing chain to form a crosslink. Since divinylbenzene has a higher reactivity it will be incorporated more rapidly than styrene or the ethylstyrenes and so as the chain length increases the proportion of divinylbenzene units incorporated will decrease as the monomer is more rapidly consumed.

Crosslinking of chains will therefore occur more frequently at the divinylbenzene rich end, and this results initially in the formation of nuclei (microgelation), but eventually sufficient intermolecular crosslinking occurs to cause macrogelation of whole droplets.

The density of crosslinks is therefore higher in the regions centred on the points of initiation i.e. the nuclei or microgels, so that each polymerizing bead consists of a mass of small, relatively highly crosslinked areas interconnected with areas of much lower crosslink density. This situation holds for all values of overall divinylbenzene content of comonomer mixtures, but of course the absolute crosslink densities in both the dense and less dense environments for a given resin, will vary considerably with the total amount of divinylbenzene used. As the amount of the latter is increased, the larger will be the intranuclear crosslink density and also the overall size of individual nuclei.

1.2.2. Gel-type resins.

If the suspension polymerization is conducted without the use of diluent (i.e. any additional solvent) the growing polymer chains are solvated only by the presence of non-incorporated monomer molecules.

This solvation obviously becomes increasingly diminished as the monomer units are used up, and eventually disappears, with the result that the nuclei aggregate as the more extended portions of the polymer chains slowly collapse together, (fig.5.)

Fig.5. Collapse of nuclei as solvating monomer is consumed in polymerization. ● = nuclei

This process of collapse is reversible, and the addition of a good solvent causes resolvation and in some cases considerable swelling of the resin. These resins are referred to as "gel-type resins" and generally the divinylbenzene content is low (10% or less, more commonly 2%).

If a gel-type resin is prepared using a high divinylbenzene content however, then a considerable amount of permanent chain entanglement occurs in addition to crosslinking, and this results in a much reduced amount of swelling on the addition of a good solvent. (Fig.6.) Addition of a poor solvent has little effect.

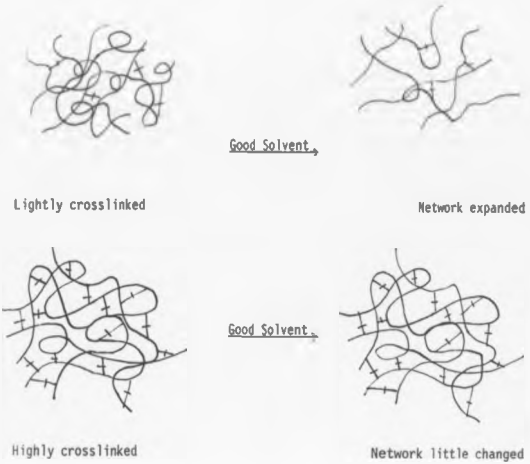


Fig.6. Effect of a good solvent on crosslinked polymeric networks.
+ = permanent crosslink.

In the dry state, these gel-type resins have little or no porosity, corresponding only to the distance between the molecular chains. On addition of a good solvent, the network of chains becomes considerably more expanded and so porosity is re-established[26]. Some lightly

crosslinked gels can absorb well in excess of their own weight of solvent (up to about 10 times) and hence this is sometimes referred to as swelling or gel porosity.

1.2.3. Macroporous and macroreticular resins

The most important way of preparing resins with enhanced porosity is by use of inert solvents or diluents in the polymerization mixture. The diluent used can be either a good solvent for both the comonomers and the product polymer[27,28], or a good solvent only for the monomers, and a precipitant for the polymer[28-30]. It is usual, when preparing these macroporous resins, to increase the overall divinylbenzene content of the comonomer mixture, so that the matrix formed has sufficient mechanical stability to retain a large volume of solvent. Crosslink ratios of 20%, or greater, are most often used.

As the polymerization proceeds, combination of chains occurs to form nuclei whose central portion is high in divinylbenzene content, and which possess outward growing chains with free radical ends. The nuclei will be swollen even if no diluent is present, since the unreacted monomers act as solvent. As the proportion of divinylbenzene is increased, the size of the nuclei is also increased, at the expense of the growing chains and this gives rise to a product with a compact and rigid structure, having considerable network entanglement in the nuclei.

However, if a solvating diluent is present (e.g. toluene, diethylbenzene,) there will be considerably less shrinkage during polymerization as the chains will be solvated at all times. As a result the nuclei are less entangled and with increasing dilution the growing

chains reach greater lengths before termination occurs. The eventual removal of the diluent after isolation of the polymer product causes a sudden collapse of the internuclear chains. (This is in contrast to the gel-type resins in which the contraction is slow and progressive during the polymerization). When all the diluent has been removed from a macroporous resin and the nuclei have aggregated, significant porosity can still remain as a result of the much larger extension of the solvated network during polymerization.

Thus these resins can absorb varying quantities of good solvents (as with gel-type resins) but can also accept some non-solvents (methanol, heptane) due to the presence of macropores.

If the polymerization is conducted in the presence of a non-solvating diluent, this will cause the precipitation of the growing polymer chains, and the changes which occur are quite complex[24,29]. The reaction temperature, concentration of crosslinking agent and diluent concentration determine when this polymer phase separation occurs. It is not possible to realise a perfectly non-solvating system however, as the unreacted monomers will solvate the growing chains to some extent.

During the phase separation, the growing chains are no longer extended and tend to aggregate into tangled masses of virtually unswollen nuclei, leaving a network of large diluent filled voids (pores) within each suspension droplet. If the resin is sufficiently highly crosslinked it will have significant rigidity and so retains its size and shape when the diluent is removed (fig.7.) Such species are known as macroreticular resins, and will absorb significant quantities of most solvents, due to the filling of available pores, but good solvents may penetrate and solvate the more highly entangled regions also.

\\ = highly entangled regions

Fig.7. Macroreticular polymer support showing rigid permanent macroporous structure.

It is of course possible to use various mixtures of solvating and non-solvating diluents and to introduce other variation by use of polar rather than non-polar diluents, to produce a wide range of porosities[28,31].

1.3. Inorganic Supports

Inorganic materials, such as silica, alumina, and molecular sieves have been investigated as macromolecular supports, of which silica has been used most frequently[32,33]. Highly porous silica can be obtained when prepared under accurately controlled conditions[34,35]. Various forms of amorphous silica exist, but all can be considered as polycondensation products of $Si(OH)_4$, orthosilicic acid. The usual methods of preparation are by acid precipitation from silicate solutions or by the hydrolysis of silicon derivatives e.g. silicon halides (SiX_4) or silicon alkoxides [$Si(OR)_4$]. Irrespective of the method of preparation, the chemical properties of these materials are very similar, although the physical properties may vary. The structure is thought to consist of tetrahedral SiO_4 units[35]. Generally these supports are obtained from commercial sources rather than in-house preparations.

Comparison of stability and loading characteristics:

(i) Organic polymeric supports are subject to considerable degradation at temperatures above approximately 150 ^{o}C; although inorganic materials are stable to temperatures far in excess of this.

(ii) Unfunctionalized polystyrene polymers are inert over a larger pH range, (but may be damaged by highly acidic conditions at elevated temperatures). Inorganic oxides may actually dissolve in highly alkaline or acidic conditions.

(iii) Mechanical stability is dependant upon a number of factors and will vary considerably according to the exact nature of the material, but in general inorganic supports are more robust. Gel-type resins are readily compressed and are not suitable for high pressure work, but do have an ability to absorb shock because of their elastomeric properties in the swollen state.

(iv) Gel-type resins have a high loading capacity, approximately up to 10 mmol g^{-1}. The maximum loading capacity of macroporous resins will vary with the nature of their preparation, but is generally considerably less than that of the gel-type resins as the entangled macromolecular chains are not readily available for functionalization; hence loadings of approximately 3 mmol g^{-1} are considered high. Silica has the lowest loading capacities of all. Functionalization is achieved by modification of surface hydroxyl groups, and as the average pore diameter of such material is low it is difficult for reagents to gain access to all the surface. Other problems, such as condensation of additional silica material in the pores means that loadings of approximately 1 mmol g^{-1} are a realistic maximum, values of 0.1 mmol g^{-1} being more common.

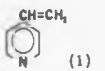
1.4. Functionalization of Supports

There are two methods for introducing a functional group onto an organic support, either by the inclusion of an appropriately functionalized monomer during the polymerization procedure, or by chemical modification of a non-functionalized pre-formed polymer. The ready availability of high quality non-functionalized supports coupled with the relative difficulty of copolymerizing a functionalized monomer has led to the former technique becoming the most popular by far. However copolymerization techniques have a number of advantages. Generally the degree of functionalization of the product is more easily controlled, and the structure of the required group can be accurately determined by analysis of the monomer before polymerization. A disadvantage in chemical modification of a pre-formed polymer will be the presence of residual functionalities from each stage of the modification procedure (assuming reactions to have less than 100% yields). The scale of these impurities can range from a point where they can be considered negligible and contribute little to the final polymer properties, to the point where they can make the final polymer useless in its application.

In the case of inorganic supports there appear to be examples only of chemical modification of the preformed materials.

1.4.1. The preparation of functionalized polymers by copolymerization

A wide variety of vinyl-derivatized molecules are commercially available, such as 4-vinylpyridine (1), or N-acryoyl morpholine (2), which can be copolymerized with styrene and divinylbenzene to produce the appropriately functionalized polymers.



(1)

(2)

However it is often necessary to synthesize a suitable monomer, and in most cases this will be a styrene derivative because of the ease with which these monomers homopolymerize or copolymerize with styrene itself.

(i) Monomer Syntheses

If the reaction conditions of the synthesis are mild, it is possible to start with the styryl group, or a substituted derivative. The formation of a Grignard reagent from p-chlorostyrene[36] or analogous reagents provides a versatile route to a range of monomers,[37,38] (fig 8).

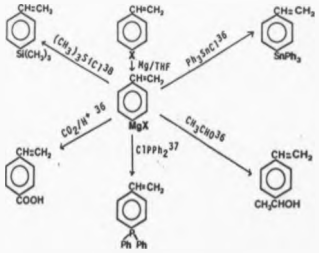


Fig.8. Reactions of p-styrylmagnesium halide.

The halostyrenes are relatively expensive and readily polymerize, therefore a free-radical inhibitor is often added to prevent polymerization of the monomers during the synthesis.[39]

Much more extreme conditions can be used if the vinyl group is protected or introduced at the end of the synthesis. 2-Phenylethylbromide is a useful starting material as it enables a wide range of aromatic electrophilic substitutions to be carried out and the vinyl group is easily regenerated by heating with a strong base to eliminate HBr.[40] (Fig.9).

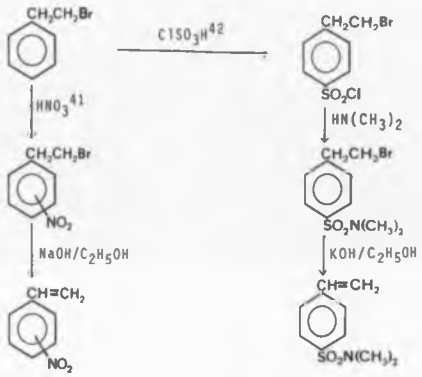


Fig.9. Use of 2-Phenylbromide as a monomer precursor.

Another commonly used route to styrene derivatives is by the dehydration of 1-arylcarbinols, a typical example being shown in Fig.10, the synthesis of p-acetoxystyrene (3).[43]

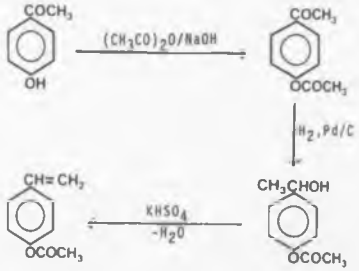


Fig.10. The synthesis of p-acetoxystyrene.

A very useful monomer is 4-chloromethylstyrene (4) which has recently become commercially available as a mixture of isomers,[44] or can be prepared to yield specifically the para isomer.[45,46]

(4)

(ii) Copolymer Structures

The functionalized monomer can be included in the monomer mix in a suspension polymerization to produce an appropriately functionalized polymer. Control over the loading of the functionality can be achieved by alteration of the ratio of functionalized monomer : styrene : divinylbenzene although altering the divinylbenzene content will of course

alter the crosslink ratio and therefore change the nature of the polymer product.

The distribution of the functionality throughout the polymer is dependant upon the reactivity towards polymerization of the monomer relative to styrene. For example, the reactivity ratios for p-styryldiphenylphosphine and styrene show the functionalized monomer to be considerably more reactive.[47] It follows therefore that the phosphine monomer will be more rapidly incorporated into the growing chains, but as its concentration is depleted, isolated segments will become more common. Also it is clear that it would be difficult to produce a copolymer with all the phosphine residues significantly isolated from each other without resorting to very low loadings. For monomers with reactivity ratios similar to styrene, the monomers will polymerize in a random fashion. The inclusion of divinylbenzene will complicate these predictions concerning functional group distribution. However it is possible to gain some idea of the resin structure in this way.

1.4.2. Chemical modification of pre-formed crosslinked polymers

It can be difficult to accurately control the loading of the resin in such chemical modifications, as not all of the reagent added may gain access to the active sites, and often large excesses are required to produce good yields. It is also difficult to characterize the changes which have taken place as only limited analytical data (elemental analysis, infrared spectroscopy) are commonly available, due to the insoluble nature of the support. Further problems arise since not all reagents can gain access into the crosslinked network. For example, aqueous solutions will not readily penetrate polystyrene resins, and also considerably more forcing conditions may be required than for a monomeric analogue.

One of the most versatile routes for chemical modification is via chloromethylation of the pre-formed polystyrene.

However chloromethylated polystyrene is now commercially available and a large number of syntheses use the commercial material as a starting point: thus reaction of the polystyrene resin with the highly carcinogenic chloromethyl methyl ether can be avoided.[48]

A variety of reactions can produce a range of different functionalized resins. (Fig.11.)

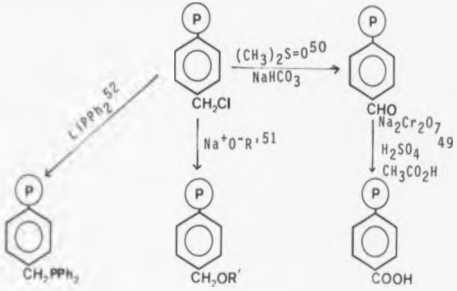


Fig.11. Some examples of further modification of chloromethyl polystyrene.

The other commonly used method for modifying polystyrene resins is via lithiation, either directly using n-butyllithium in N,N,N,N-tetramethylethylene diamine (TMEDA) or indirectly by lithiation of an already halogenated resin. Direct lithiation generally gives rise to a low-loaded resin ($\sim$25%),[53] with substitution in either the meta or para positions.[54]

The lithium-halogen exchange route allows higher degrees of functionalization, and most investigations use bromination as the first step.

Early work used ferric chloride as the catalyst for bromination[53], but thallic acetate gives cleaner results and better reproduceability[53]. Further modification yields a variety of functionalities, some of which are illustrated in fig. 12.

The generation of the diphenylphosphine group on the polymer support leads to one of the most widely used functionalities in the study of polymer-supported catalysts[2,56]. The diphenylphosphine unit has also been generated by the inclusion of p-styryldiphenylphosphine as comonomer in styrene/divinylbenzene suspension polymerizations[57,58] and so therefore its uses on the polymer support are well documented.

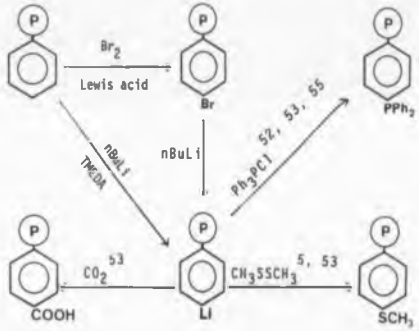


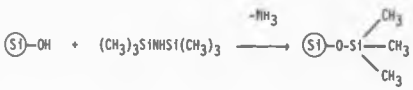
Fig. 12. Some examples of further modification of lithiated polystyrene.

There are a vast number of other transformations possible for the introduction of functional groups onto pre-formed polystyrene polymers, though chloromethylated or lithiated polystyrenes are amongst those most often used.

It is of course possible to combine the methods described in sections 1.4.1. and 1.4.2 i.e. by inclusion of a functionalized monomer in the polymerization mixture, followed by further modification of the functionalized polystyrene.

1.4.3. Modification of inorganic oxides

Inorganic oxides such as silica have an abundance of hydroxyl groups at their surface which are accessible for modification. Several methods are available, but the most commonly used is the reaction of an appropriate silane molecule of the type $RSiX_3$ (where X is a readily hydrolysable group e.g. OR,OCOR,Cl,NH_2) with the silica support[32]. The Si-O-Si linkage formed is very strong and the Si-C bond formed at the surface is more hydrolytically and thermally stable than either an Si-O-C or Si-N-C unit. Since unreacted surface hydroxyl groups may give rise to adsorption problems, it is usual to subsequently silylate an already functionalized support with hexamethyl disilazane.



2. Isocyanides .

The isocyanide ligand is an extremely versatile one, being able to complex both normal and low oxidation state metals. It is isoelectronic with carbon monoxide, but the latter does not form stable complexes with the higher oxidation state metals and also being diatomic, cannot be anchored to a polymer support. The presence of the R group on the isocyanide makes this an ideal choice.

Isocyanides are also known as "isonitriles" and "carbylamines", although the latter is rarely used. "Isonitrile" is still often used, but "isocyanide" is the name adopted by I.U.P.A.C. and is used in " Chemical Abstracts" indices.

2.1 Synthesis of isocyanides

Although isocyanides have been known for over a century, it is only in the last 20-30 years that detailed attention has been paid to these compounds. When first synthesized, isocyanides were mistakenly thought to be cyanides, and further studies were often discontinued due to the penetrating odour. However, by 1870, isocyanides were recognised as distinct compounds, and were described as "isomers of the ordinary nitriles".[59]

There are several methods of synthesizing the isocyanide ligand, but the most commonly used method is the dehydration of the appropriate formamide.

$$R\text{-}N{\equiv}C \leftrightarrow R\text{-}N{=}C:$$

$$R\text{-}NHCHO \xrightarrow{-H_2O} R\text{-}N{\equiv}C$$

This is a general method which can be used for a large number of isocyanides. Prior to 1965, approximately 40 isocyanides had been reported in the chemical literature, but with the publication of an article by Ugi,[60] detailing the dehydration method, a further 240 were described. Several dehydrating agents have been used, generally being an acylating agent and a base, but those most commonly referred to are:

(i) p-toluenesulphonyl chloride and pyridine[61]

(ii) phosgene and triethylamine[60]

(iii) diphosgene and triethylamine[62]

Experimental details for all three methods are included in chapter two; method (i) using p-toluenesulphonyl chloride was the method preferred for the polymer-supported isocyanide.

2.2 Synthesis of metal-isocyanide complexes

Most recent work has concentrated on mixed and homoleptic low valent mono- and polymetallic complexes of isocyanides, whereas earlier work was concerned more with complexes in which metals were in their higher oxidation states. A brief discussion of some of this older work is given here, as the more recent work is discussed in chapter three in comparing homogeneous reactions to those occuring on the polymeric support.

A considerable amount of work on low valent metal-isocyanide complexes arises from the preparation of the latter by substitution of the carbonyl group in many metal-carbonyl complexes. These complexes frequently retain one or more carbonyl group, resulting in a mixed ligand product. Other ligands, such as phosphines are also found in these mixed compounds, but neither of these will be discussed in detail. The reactions of alkyl or aryl isocyanides with metal salts in solution are more closely related to the reactions carried out using the polymer-supported isocyanide. The older work ,dating around the mid 1950's, is

principally concerned with the reaction of isocyanides with metal salts. A considerable amount of this early work was carried out by Malatesta and is well documented[63,64]. A further review by Ugi[59] is orientated towards the organic chemistry of isocyanides, and two later reviews have been published on isocyanide-metal complexes[65,66]. The field of isocyanide-metal chemistry has now become considerably expanded and a detailed review of all areas is not possible here. The work described will therefore be limited to those metal-isocyanide complexes which have some similarity to the reactions studied using the polymer-supported isocyanide.

2.2.1 Chromium, Molybdenum and Tungsten.

Isocyanide complexes of the group IIB metals are prepared by two general methods:

(i) $M(CNAr)_6$ M=Cr,W,Mo;

prepared by the reaction of the metal salt with an aryl isocyanide, either in the presence of a reducing agent or with valence disproportionation.

e.g. $3\ Cr(OAc)_2 + 18RNC \rightarrow Cr(CNR)_6 + 2[Cr(CNR)_6][OAc]_3$

The acetate product was not isolated, but the experimental quantities for the reactants and other products were in close agreement with the proposed equation.[63,67] For this reaction, the molybdenum-isocyanide complex is less stable than the corresponding chromium complex, and for tungsten the reaction requires the slow addition of WCl_6 to a mixture of isocyanide, magnesium powder, in anhydrous alcohol, containing a few drops of acetic acid.[68]

(ii) $M(CO)_{6-x}(RNC)_x$ M=Cr,Mo,W

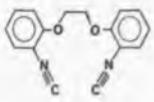
x=1-3 for R=Bu^tNC; others give mono- and di- substituted products.

Various catalysts have been employed to increase the yield and degree of substitution in these reactions, for example cobalt chloride.[69] In a recent review, Singleton claims complete substitution of isocyanide, with

yields greater than 90% for these metals.[66]

2.2.2 Manganese and Rhenium

The reaction of anhydrous manganese(II) iodide with isocyanides has been reported to yield complexes of the type $[Mn(CNR)_6]I$ [70] although generally Malatesta reports that manganese(II) salts do not show any tendency to react with isocyanides.[63] Complexes of the type $Mn(CNR)_6X_2$ have been prepared by nitric acid oxidation of the corresponding manganese(I) complex, followed by precipitation with a suitable counter-ion, (R=Ph, Et, Bu^t; X=PF_6^-, NO_3^-). However a recent report details the reaction of an anhydrous manganese(II) salt with t-butyl isocyanide in dry toluene to yield $MnX_2(CNBu^t)$, (X=Cl, Br, I, SCN).[71] The bidentate ligand shown below has also been used to complex manganese.[72]



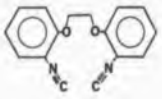
Only a small number of rhenium-isocyanide complexes have been reported, although one example of an anion-containing isocyanide ligand exists, in $[ReCl_5(CNMe)]^-$ prepared from $[Re_2Cl_8]^{2-}$ with methyl isocyanide in methanol.[73] A variety of cluster compounds are formed from the reaction of K_2ReI_6 and excess isocyanide, dependent on the solvent and reaction conditions used.[66]

2.2.3 Iron, Ruthenium and Osmium

Iron(II)-isocyanide complexes of the stoichiometry $Fe(CNR)_4X_2$ (R=alkyl or aryl; X=Cl, Br, I) are isolated in two forms, a green/blue complex, sparingly soluble (in organic sovents), obtained by rapid precipitation from cold alcoholic or aqueous solutions; and a brown/yellow, very soluble complex, which is obtained by refluxing the former in solvent, or by precipitation from hot solution.[74] These two forms were assumed to be cis/trans isomers.

The direct reaction of p-tolyl isocyanide and iron(II) perchlorate, without solvent, yielded a dark oily tar and a stable, crystalline product, $[Fe(CNC_7H_7)_6][ClO_4]_2$, and treating $Fe(CNC_7H_7)_4Cl_2$ with excess sodium perchlorate in refluxing acetone gave $[Fe(CNC_7H_7)_5Cl]ClO_4$ as the product.[75]

Other $FeCl_2(CNR)_4$ complexes have been prepared by the reaction of hydrated ferrous chloride with a bidentate isocyanide ligand (also mentioned in section (b)) in methanol[76] as shown below:



+ $FeCl_2.4H_2O$

MeOH

cis-$FeCl_2$(DiNC)$_2$ + trans-$FeCl_2$(DiNC)$_2$

orange blue

The reaction of iron carbonyls with isocyanides succeeds with partial substitution of ligands, to produce $Fe(CO)_{5-n}(RNC)_n$ (n=1,2) using $Fe(CO)_5$; for example $Fe(CO)_4CNC_6H_{11}$ was produced upon ultraviolet irradiation of $Fe(CO)_5$ and cyclohexyl isocyanide.[77] The reaction of $Fe_3(CO)_{12}$ with $CN(CH_2)_nNC$ (n=2,6) produced exclusively the dimer $[Fe(CO)_4]_2CN(CH_2)_nNC$. Long reaction times and forcing conditions illustrate the fairly inert nature of the metal carbonyl. However, stepwise substitution products $Fe(CO)_{5-n}(CNR)_n$ (n=1-5) have been successfully obtained with high yields and short reaction times by use of catalysts such as cobalt chloride, activated carbon, or metals on metal oxide or carbon supports.[66]

In the case of ruthenium, Ru(II) derivatives of the general formula $RuX_2(CNR)_4$ (R=alkyl or aryl; X=Cl, Br, I) were reported by Malatesta and Sacco.[78] The dichloride and dibromide complexes were prepared by boiling an alcoholic mixture of the metal chloride or bromide and the isocyanide, but the iodide was prepared by reaction in pure isocyanide. All these complexes were found to exist in two forms, presumed to be cis and trans isomers.

The zerovalent complexes $Ru(Bu^tNC)_5$ and $Ru_2(i\text{-}PrNC)_9$ have also been reported, as well as several examples of mixed ligand complexes.[66]

An attempt to produce $Os(Bu^tNC)_5$ from $[Os(cod)Cl_2]_n$ with Na/Hg in the presence of excess isocyanide yielded only the product $[Os(Bu^tNC)_3(cod)]$,[79] although the complex $Os(CNxylyl)_5$ has been prepared by the Na/Hg reduction of the metal halo-isocyanide. Substitution reactions on the cluster $M_3(CO)_{12}$ by isocyanides in high boiling solvents have given up to tetrasubstitution products for osmium. Preparation of the chloro-compounds $[OsCl_2(CNR)_2]_x$ (x>2), and cis/trans isomers for $OsCl_2(CNR)_4$ (R=Bu^t,xylyl) were also reported.[66].

2.2.4 Cobalt, Rhodium and Iridium

Stable cobalt(II)-isocyanide complexes are formed from the reaction of isocyanides with cobalt halides and thiocyanates. Sacco and Freni[80] isolated two types of complexes from these reactions, $CoX_2(CNR)_2$ and $CoX_2(CNR)_4$ (R=CH_3; X=Cl, Br, I, SCN), and similar results were obtained by Malatesta and Giuffre[81] (R=C_6H_5). However the situation for cobalt(II) perchlorate is complex. Sacco first investigated the reaction of the latter with isocyanides which yielded a greenish-blue complex $[Co(RNC)_5][ClO_4]_2$, (R=phenyl, p-tolyl, o-tolyl). The reaction of cobalt(II) perchlorate was further studied by Sacco and Freni[80] who discovered two forms for the product, one blue and paramagnetic, the other red and diamagnetic. Two forms for the product, $[Co(PhNC)_5][ClO_4]_2$ were also isolated by two later groups of workers,[82, 83] but these forms were discovered to correspond to a hydrated blue form and a yellow anhydrous form. A red complex was also isolated and was found to be a dimer $[Co_2(RNC)_{10}][ClO_4]_4$, (R=Me, Et,); which is presumably the red complex obtained by Sacco and Freni.

Isocyanide analogues of $Co_2(CO)_8$ were recently prepared independently by two groups. Stone and co-workers[84] synthesized $Co_2(CNBu^t)_8$, whilst Yamamoto and Yamazaki[85,86] prepared $Co_2(RNC)_8$ (R=2,6-xylyl, 4-Br-2,6,-xylyl, 2,4,6-mesityl) by treating $Co_2(CO)_8$ with the appropriate isocyanide at room temperature. The structure is similar to that described for $Rh_2(CNR)_8$ (see later).

The reaction of hydrated rhodium chloride with isocyanide in alcoholic solution was investigated by Malatesta and Vallarino.[87] A violet, crystalline product $[(p\text{-}ClC_6H_4NC)_4Rh]Cl$ was found when p-chlorophenyl isocyanide was used but the addition of precipitating agents

(perchlorate or hexafluorophosphate) was required in the case of phenyl, p-tolyl and p-methoxyphenyl isocyanides. The fact that the reduction of the metal is due to the isocyanide rather than to the presence of ethanol in these reactions, is suggested by similar results (i.e. reduction to Rh(I)), found in the reaction of methyl isocyanide with hydrated rhodium chloride.[88]

Rhodium(I)-isocyanide complexes $[Rh(RNC)_4]^+$ were also prepared by the reaction of the dimer $[Rh(CO)_2Cl]_2$ with isocyanides, (R=p-$MeOC_6H_4$, p-MeC_6H_4, p-ClC_6H_4)[87]. When a reduced amount of isocyanide was used, the intermediate $Rh(CO)(CNR)_2Cl$ was discovered.[89] The phosphine-isocyanide rhodium complex $Rh(PPh_3)_2(CNCH_3)Cl$ was obtained from the reaction of methyl isocyanide with $Rh(PPh_3)_3Cl$, and is reported to reversibly add oxygen although the product complex is not isolated.[90] However the analogous complexes, $RhL_2(CNR)X.O_2$ are isolable, (R=C_6H_{11}, p-$C_6H_4CH_3$, Bu^t; L=PPh_3, $AsPh_3$; X=Cl, Br, I).[91]

The complex $Rh_2(RNC)_8$ has been prepared by the reduction of $Rh(CNR)_4Cl$ by Na/Hg;[79] having a structure in which the two rhodium atoms are linked by an isocyanide-bridged metal-metal bond. The carbonyl derivatives $Rh_4(CO)_{12-n}$(p-tolyl isocyanide)$_n$ (n=1,2,4,) and $Rh_6(CO)_{10}$(p-tolyl isocyanide)$_6$ have also been prepared.[92]

For iridium, the reaction of $Ir_4(CO)_{12}$ with t-butyl isocyanide produced a complex $Ir_4(CO)_{11}(Bu^tNC)$ whose infrared spectrum did not show the presence of any bridging carbonyl ligands.[93] Although several examples of mixed ligand complexes exist for iridium, (particularly triphenylphosphine and its derivatives), no examples of homoleptic iridium-isocyanide complexes have been found.[65]

2.2.5 Nickel, Palladium and Platinum

Although Malatesta states that a lively and very exothermic reaction takes place between isocyanides and alcoholic solutions of nickel(II) salts, very few nickel(II)-isocyanide complexes have been reported. Malatesta[94] gives formulae of the type $NiCl_2(CNR)_2$ to the products of the reaction between anhydrous nickel chloride and isocyanides ($C_5H_{11}NC$, C_6H_5NC), although the products are described as brown powders that cannot be re-crystallized, and on heating decompose into a black molten mass; thus these characteristics make such formulation doubtful.

Virtually all the work on nickel-isocyanide complexes centres in the nickel(0) species. These complexes have been formed both by reduction of nickel(II) in the presence of isocyanides[63] and by the reaction of isocyanides with nickel tetracarbonyl[63]. In the case of aryl isocyanides, complete substitution of the carbonyl ligands was observed, but with methyl isocyanide the product was $Ni(CO)(CNCH_3)_3$. Other $Ni(RNC)_3L$ mixed ligand complexes have been reported from the reaction of $Ni(RNC)_4$ (R=t-butyl, isopropyl, or cyclohexyl) with L^1 (L^1=phosphine,arsine)[65].

In a review published in 1983,[66] only one homoleptic nickel(II)-isocyanide complex is mentioned. The complex $[Ni(CNBu^t)_4][ClO_4)_2$ was prepared from nickel perchlorate and t-butyl isocyanide in ethanol[95]. The complex is synthesized by dehydration of a precursor complex $[Ni(CNBu^t)_4(H_2O)_2(ClO_4)_2]$. The lack of nickel(II)-isocyanide complexes may be due to the fact that nickel salts are known to catalyse isocyanide polymerization.[96]

Malatesta[63] reports that palladium halides react readily with aryl isocyanides, yielding products which analyse as $PdX_2(CNR)_2$ R=p-anisyl, p-tolyl; X=Cl, Br, I) no isocyanide derivatives of palladium(II) salts

with non-coordinating anions could be prepared, both $[Pd(CNR)_2]^{2+}$ and $[Pd(CNR)_4]^{2+}$ being described as unstable. This is in contrast to the results obtained by Miller and Balch,[97] who isolated $[(CH_3NC)_4Pd]^{2+}$ as the hexafluorophosphate salt.

The preparation of a palladium(I) complex is described in the reaction of a palladium(0) and a palladium(II) complex, as shown below:[98]

$$Pd(dba)_2 + PdCl_2(C_6H_5CN)_2 + 4Bu^tNC \xrightarrow{C_6H_5Cl} [Pd_2Cl_2(Bu^tNC)_4] + 2dba + 2C_6H_5CN.$$

dba=dibenzylidene acetone.

Palladium(0)-isocyanide complexes have been prepared by Malatesta[99] by the reduction of $(RNC)_2PdI_2$ in strongly alkaline solution (alcoholic potassium hydroxide), but only if more than 2 moles of isocyanide per mole of $(RNC)_2PdI_2$ are present, (R=phenyl, p-methylphenyl, p-methoxyphenyl). The later availability of suitable metal(0) complexes has led to further work in more recent years and is discussed in chapter three.

The blue-violet complex described as $[Pt(C_6H_5NC)_2Cl_2]_x$ was first prepared by Ramberg in 1907,[100] and also isolated later by Malatesta and Bonati[101] from the reaction of aqueous potassium tetrachloroplatinate(II) and phenyl isocyanide. In a series of similar experiments with other isocyanide ligands, the authors found that two types of compound resulted: those which were blue and insoluble in organic solvents (R=phenyl,p-tolyl), and also those which were red and soluble in common organic solvents (R=p-anisyl,cyclohexyl). The authors describe the products in the form $[Pt(CNR)_4][PtCl_4]$ and state that the difference in the two types is probably due to the existence in the blue compounds of a strong metal-

metal interaction which is not possible when the organic group has a bigger steric requirement, as with p-anisyl or cyclohexyl isocyanide. The salts of these ligands are red, similar to the colour of the $[PtCl_4]^{2-}$ ion. All the $[Pt(CNR)_4][PtCl_4]$ compounds prepared by Malatesta and Bonati were transformed into their soluble cis-$Pt(CNR)_2Cl_2$ isomers (yellow) on refluxing in chloroform solution, or in some cases on prolonged heating to 110-150 °C, in the dry state. The infrared isocyanide stretching frequencies observed for these compounds[101] were in the range 2205-2270 cm^{-1}, the frequencies being considerably higher than in the corresponding free ligand. This is consistent with other reports for such metal-isocyanide complexes, and is discussed in more detail in chapter three.

2.2.6 Copper, Silver and Gold.

Four products are described for the reaction of copper(I) chloride with phenyl or p-tolyl isocyanide when the conditions used are varied.[102] The products $[Cu(CNAr)_4Cl]$,$[CuCl(CNAr)_3]$, $[CuCl(CNAr)_2]$ and $[CuCl(CNAr)]$ can be interconverted by techniques such as heating in water or solvent.[63,102] The product of a similar reaction[103] in alcoholic solution was determined to be the tetra-coordinated species, $[Cu(p\text{-}CH_3C_6H_4NC)_4]ClO_4$.

Copper-isocyanide complexes which contain a second ligand have also been described. The white complex, $C_5H_5Cu(CNCH_3)$ was prepared in 57% yield from $(CH_3NCCuI)_4$ and C_5H_5Tl.[104] A similar product, $C_5H_5Cu(CNBu^t)$ was obtained from the reaction of Cu_2O, $CNBu^t$ and C_5H_6. A product of different stoichiometry, $C_9H_7Cu(CNBu^t)_3$, was obtained when indene was used in place of C_5H_6,[105,106] the preparation of $Cu(acac)(CNPh)_2$ has been described from copper(I) acetylacetonate (acac) and phenyl isocyanide.[107]

Only a small amount of work detailing the preparation of silver-isocyanide complexes is found in the literature. Early work on the alkylation of silver cyanide yields the complex AgCN.CNR as product, this being one of the first isocyanides to be discovered. [63] This method of preparation of isocyanides is now rarely used.

Klages and Monkmeyer[102] describe the preparation of both di- and tetra-coordinated products from the reaction of silver nitrate with p-tolyl isocyanide, in contrast to a similar reaction reported by Sacco,[103] in which only the isolation of $(p\text{-}CH_3C_6H_4NC)_4AgClO_4$ is listed. Several more recent examples of silver-isocyanide complexes are mentioned in chapter three.

The isolation of gold(III) and gold(I)-isocyanide complexes has been reported by Sacco and Freni.[108] The complexes of the type $(RNC)AuCl_3$ were stable when recrystallized, but were reduced to (RNC)AuCl in the presence of excess isocyanide, (R=p-MeC_6H_4, Ph). A third type of complex is also described, $[(RNC)_4Au]Cl$ was prepared by heating $(RNC)AuCl_3$ with excess isocyanide in ethanol. These latter complexes were not stable in solution, decomposing to yield (RNC)AuCl. Later work on gold-isocyanide complexes, as described in chapter three, reports only the isolation of reduced Au(I) complexes.

A recent example of the formation of a gold(I)-isocyanide complex by ligand displacement is seen in the addition of phenyl or p-tolyl isocyanide to $cis\text{-}[Au(C_6F_5)_2(OEt_2)_2]ClO_4$. This leads to the isolation of $cis\text{-}[Au(C_6F_5)_2(CNR)_2]ClO_4$ complexes as white solids which are air and moisture stable at room temperature. These complexes also undergo addition reactions with hydrazines.[109]

2.2.7 Zinc, Cadmium and Mercury.

Very few examples of metal-isocyanide complexes exist for zinc and cadmium. There are several reports of mercury-isocyanide reactions, but examples of these are discussed in chapter three, and will not be duplicated here.

Many other examples of metal-isocyanide complexes exist, including many mixed ligand complexes; this being only a brief review to illustrate the versatility of the isocyanide by detailing some of the known reactions.

2.3 Reactions of metal-isocyanide complexes and ligands.

Although the earlier sections have concentrated on the synthesis of metal-isocyanide complexes, an extensive array of literature reports detail the reactions of metal-isocyanide complexes and also reactions of the ligand itself, therefore a brief mention of some of these reactions is given here.

2.3.1. Oxidative addition reactions.

Oxidative additions have been performed on cations such as $[M(CNR)_4]^+$ (M=Rh, Ir) using a variety of reagents, for example: proton acids, halogens, alkyl and aryl halides, $HgCl_2$, and $SnCl_2$. In most cases the products are from a two electron oxidative addition. For example, addition of I_2 to $[Rh(Bu^tNC)_4]BF_4$ afforded the octahedral species $[Rh^{III}(Bu^tNC)_4I_2]BF_4$, the iodine atoms occupying trans positions.[110] Several other examples are also quoted in the review by Singleton and Oosthuizen.[66]

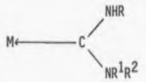
2.3.2. Nucleophilic addition by alcohols and amines

In these reactions the O-H or N-H bonds of alcohols or amines are added across the C≡N bond in isocyanides, to form carbene complexes. The general reactions are represented below:

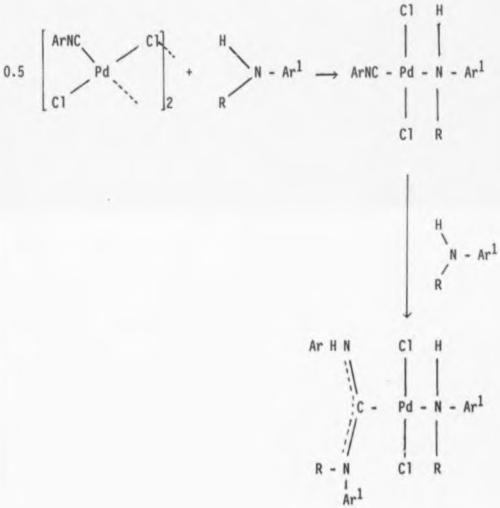
$$M\text{-}C{\equiv}N\text{-}R + HOR^1 \longrightarrow M{=}C(OR^1)\text{-}NHR \quad \text{for alcohols,}$$

$$M\text{-}C{\equiv}N\text{-}R + HNR^1R^2 \longrightarrow M{=}C(NR^1R^2)\text{-}NHR \quad \text{for amines}$$

A general reaction pathway for the amino addition is shown in chapter three, to yield the carbene product:



The formation of carbene derivatives from the reaction of $[PdCl_2(CNAr)]_2$ with aromatic amines was studied by Calligaro et al,[111] who found that initial halide-bridge splitting was followed by reaction with a second molecule of amine with the isocyanide to yield the carbene complex, as shown below:



The reactions proceed via initial nucleophilic attack at the isocyanide carbon and although carbon monoxide also undergoes such attack, stronger nucleophiles and more forcing conditions are required.

2.3.3 Insertion reactions

Isocyanides commonly undergo insertion reactions into a variety of metal-carbon bonds, as well as metal-hydride, metal-oxygen, metal-nitrogen, metal-sulphur and metal-halogen bonds. Examples of all these reactions are found in the review by Singleton and Oosthuizen.[66]

The insertion reaction can be regarded as an alkyl (or aryl, hydride, oxygen etc) migration as shown in the general reaction below.

For example, the reaction of $Re^{VI}Me_6$ with $CNBu^t$ proceeds with concomitant reduction to give $Re^{II}(CNBu_t)_2\{CMe{=}NBu^t\}_3$.[66] The reaction of $Zr(CH_2CMe_3)_4$ with $CNBu^t$ proceeds without reduction to give $Zr(CH_2CMe_3)_3(CNBu^t)\{C(CH_2CMe_3){=}NBu^t\}$.[66]

The reaction of $Pt(PPh_3)_2(R)X$ ($R=CH_3$, C_6H_5; X=Cl, Br, I) and methyl isocyanide proceeds via initial halide displacement, confirmed by the isolation of the intermediate, (A).[65]

$$PtL_2(R)X + CNCH_3 \longrightarrow [PtL_2(CNCH_3)R]X \quad (A)$$

$$\downarrow$$

$$PtL_2\{C(=NCH_3)R\}X$$

$L=PPh_3$ $R=CH_3$ X=Br,I

Carbon monoxide also undergoes insertion reactions but there are two main differences seen for the reactivity of the latter . Carbon monoxide does not undergo multiple insertions, which are often seen for isocyanides, and also carbon monoxide does not insert into metal-hydride bonds, in contrast to the isocyanide. Isocyanide insertion into the Pt-H bond in trans-$[PtH(CNC_6H_4Me\text{-}p)L_2]Cl$ ($L=PEt_3$, PMe_2PH) gave the product[66] trans-$PtCl(CH=NC_6H_4Me\text{-}p)L_2$.

From the examples quoted it can be seen that the isocyanide is extremely versatile in both organic and organometallic reactions. Although many examples exist of polymer-supported ligands (particularly for triphenylphosphine and especially in the field of polymer-supported catalysts), no examples of polymer-supported isocyanides were reported until very recently. The combination of the advantages of a polymer support, coupled with the versatility of the isocyanide ligand, should potentially pave the way for further extensive studies.

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CHAPTER 2: MONOMER SYNTHESIS, POLYMERIZATION AND FURTHER MODIFICATION

2.1. Introduction

Although the most commonly employed method of functionalizing polymers is by modification of pre-formed, commercially available polystyrene, it was decided to approach the problem of functionalized polymers by polymerization of suitably functionalized styrene monomers. There are several reasons for this choice.

(i) Polymer Laboratories, the collaborating body, have many years experience in controlling polymerization conditions to yield styrene-divinylbenzene copolymers of well-defined pore size and particle size. Their expertise in polymer fabrication was available to us for the production of functionalized polystyrenes from functionalized monomers.

(ii) As it was hoped to evaluate the functionalized polymers in various applications in metal complexation (for example in affinity chromatography, metal extraction/recovery and catalysis) it is necessary to control both the crosslink ratio (controls the mechanical stability of the polymer), and the loading of the functional group according to its projected use. For affinity chromatography, a high crosslink ratio is required to give the necessary mechanical stability so that the polymer can be packed into a column and used under high pressures. A high loading of the functionality will also be necessary. Less mechanical stability is necessary for catalytic work and considerably lower loadings are required. For metal extraction a high loading would be necessary and the crosslink ratio could be tailored to the physical/mechanical needs of the process. It is often difficult to control the loading when modifying pre-formed polystyrene[1]. It was therefore considered better to produce resins in-house, where careful control could be kept over these variables.

(iii) By including the functionalized monomer in the polymerization mix, the purity of the functionality can be controlled (by recrystallization, distillation etc. before use). This is in contrast to the product from the modification of polystyrene where in a multistage synthesis, some residual functionalities will remain from each stage in the synthesis. These may create problems, depending upon the final use of the polymer and the nature of the residual functionality.

In addition, as analysis techniques are limited, due to the insoluble nature of the polymer, it is difficult to determine the extent of functionalization achieved by modification of pre-formed polystyrene. Elemental analysis such as C, H, N analysis can really only be useful in the first step of a multi-step synthesis as the effect of residual functionalities will be seen in subsequent analysis figures but without any indication of the proportion of "old" and "new" functionality if both contain nitrogen, for example.

2.2. Results and Discussion

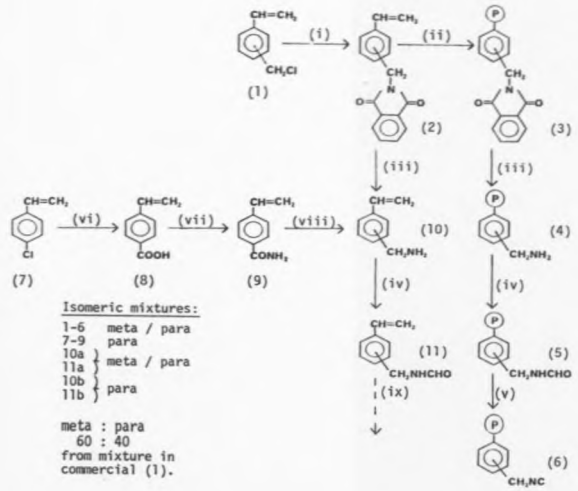
(1.) Monomer Syntheses

The general approach to the synthesis of isocyanide-functionalized polymers via polymerization of suitably functionalized monomers is shown in figure 1.

Although in general free-radicals have failed to polymerize isocyanides[2], some isocyanides polymerize spontaneously on storage (for example vinyl isocyanide)[3] and most isocyanides tend to polymerize at elevated temperatures[4]. With the additional potential industrial problem of working with foul smelling and toxic liquids, it was initially decided to attempt the polymerization of the isocyanide precursor, the formamide (11a, 11b) which may be synthesized via two routes.

(a) From p-chlorostyrene (7) :

Several attempts at the synthesis of p-vinylbenzoic acid (8) following the literature procedure[5] gave little or none of the desired product. This problem is the result of two factors: (a) the reaction temperature must be kept below 60 ^{o}C at all times, to prevent polymerization of the vinyl group and (b) as the carboxylic acid is not very soluble in most common organic solvents (e.g. THF, ether, dichloromethane, ethyl acetate) it is precipitated along with the magnesium by-products when the excess Grignard reagent is neutralized. Only an extremely small amount, if any, remains in solution and can be extracted following the literature procedure. A good yield was eventually obtained by careful extraction of the insoluble products produced on hydrolysis of the excess Grignard reagent. As poor recovery of product was observed using the literature method of recrystallization from 20% ethanol, and as



Isomeric mixtures:

1-6	meta / para
7-9	para
10a, 11a	meta / para
10b, 11b	para

meta : para
60 : 40
from mixture in commercial (1).

Reagents:

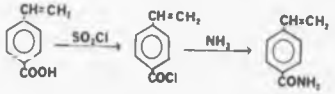
(i) $KNC_8H_4O_2$ / DMF
(ii) Benzoyl peroxide initiated copolymerization, (& styrene & divinylbenzene)
(iii) $NH_2NH_2.H_2O$ / C_2H_5OH
(iv) $HCO_2C_2H_5$
(v) $p\text{-}CH_3C_6H_4SO_2Cl$ / C_5H_5N
(vi) Mg / THF; CO_2
(vii) $SOCl_2$; NH_3
(viii) $LiAlH_4$ / Et_2O
(ix) Attempted copolymerization as in (ii)

Figure 1.

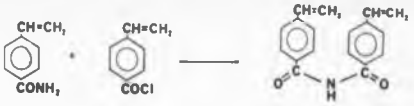
General approach to the synthesis of isocyanide-functionalised polystyrene resins.

the product was also difficult to dry, absorbing more than its own weight of water, the spectroscopically pure "crude" product was used without further purification.

Conversion of the acid (8) to the amide (9) following the literature procedure[6] (reaction with thionyl chloride followed by reaction with ammonia in benzene solution) also gave poor yields. N.m.r. studies showed that the acid chloride intermediate was prepared satisfactorily (figure 2).



Subsequent reaction of the acid chloride with dilute aqueous ammonia gave substantial amounts of a second component. The n.m.r. spectrum (figure 3) of the crude product shows evidence of a compound exhibiting phenyl resonances, and an additional set of resonances due to a vinyl group. It was thought that the acid chloride formed then reacted with the amide as it was produced, to yield an imide.



It should be noted that the proportions of the two products shown on the n.m.r. spectrum (i.e. mainly amide (9)) are not truly representative of the amounts found in the crude product. A considerable amount of insoluble material remained in the sample prepared for n.m.r. spectroscopy; thus the yield of amide from this reaction is lower than the spectrum suggests. This was confirmed by very poor yields (~ 30%) and the presence of a large amount of insoluble material during recrystallisation.

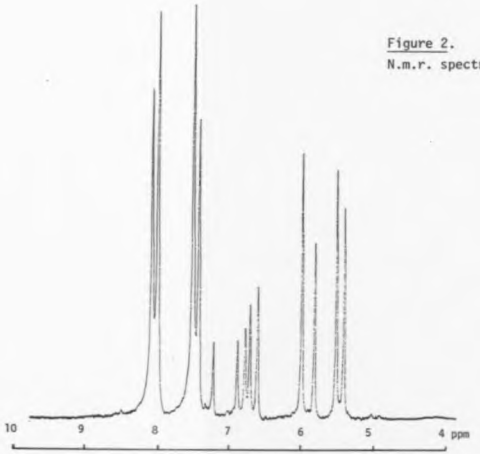


Figure 2.
N.m.r. spectrum of p-vinylbenzoic acid chloride.

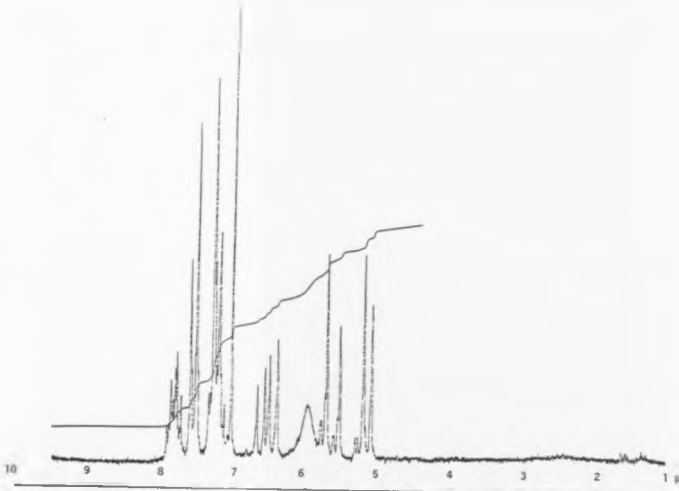


Figure 3. N.m.r. spectrum of crude p-vinylbenzamide, showing the presence of a second component.

To suppress imide formation, the acid chloride was added dropwise to excess anhydrous liquid ammonia, and a considerable improvement in yield was observed, (40% → 70%). Although the use of concentrated aqueous ammonia also suppressed imide formation, poorer yields were obtained due to the slight water solubility of the amide (9). Pure amide (9) could be obtained by recrystallization from aqueous alcohol[6], but this was generally not carried out since the Soxhlet extraction used in the conversion to the amine (10b) extracts amide (9) and leaves behind the ammonium chloride by-product. Good yields of amine (10b) can be obtained by this procedure; the conversion from amide (9) to amine (10b), using lithium aluminium hydride in ether, can be followed by removing samples from the Soxhlet thimble for n.m.r. spectroscopy until the spectrum shows no amide present.

The direct reaction of pure p-vinylbenzamide (9) with lithium aluminium hydride in ether gave poor yields of amine (35%). This was due in part to the low solubility of the amide in ether, as illustrated by the improvement in yield found when the technique of Soxhlet extraction was incorporated into the method, either for pure amide (only), (yield 64%) or for the amide/ammonium chloride mixture (yield 59%).

Some further reaction of p-vinylbenzylamine was observed, due to some reduction of the vinyl group by lithium aluminium hydride. This was estimated to be approximately 13% of the total product from the n.m.r. spectrum (figure 4), and is evident in the appearance of resonances due to an ethyl group in both the ^{1}H and ^{13}C n.m.r. spectra (figures 4 and 5). In order to confirm this, a sample of p-vinylbenzylamine (10b) was hydrogenated and the distilled product, p-ethylbenzylamine, had ^{1}H and ^{13}C n.m.r. spectra identical to that of the ethyl impurity (figures 6 and 7).

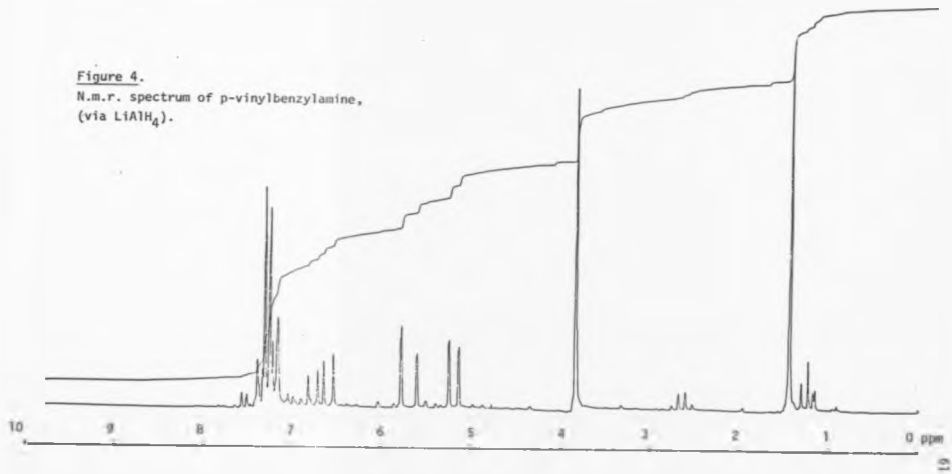
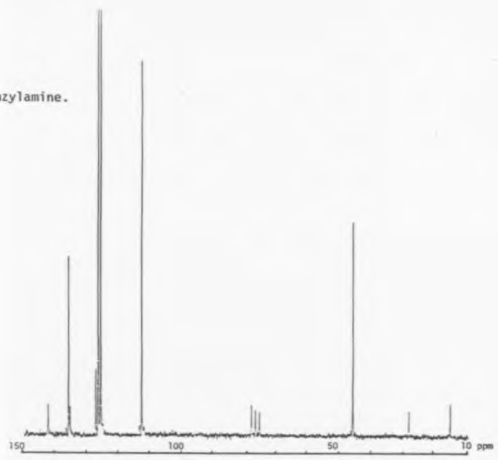


Figure 4.
N.m.r. spectrum of p-vinylbenzylamine, (via $LiAlH_4$).

Figure 5.
^{13}C n.m.r. spectrum of p-vinylbenzylamine.



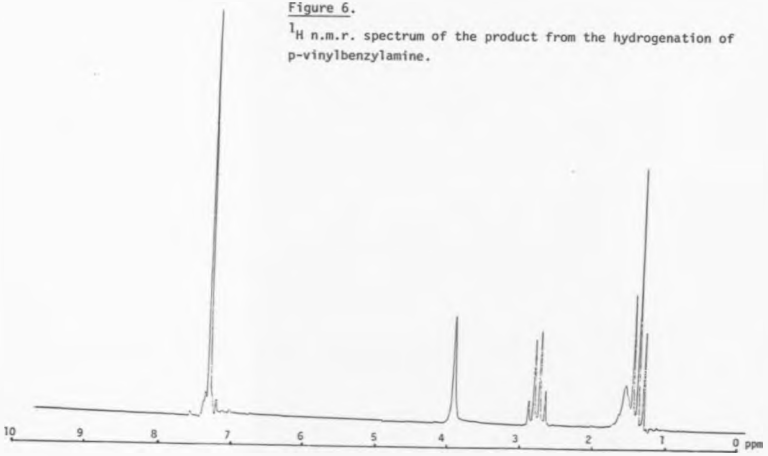


Figure 6.
^{1}H n.m.r. spectrum of the product from the hydrogenation of p-vinylbenzylamine.

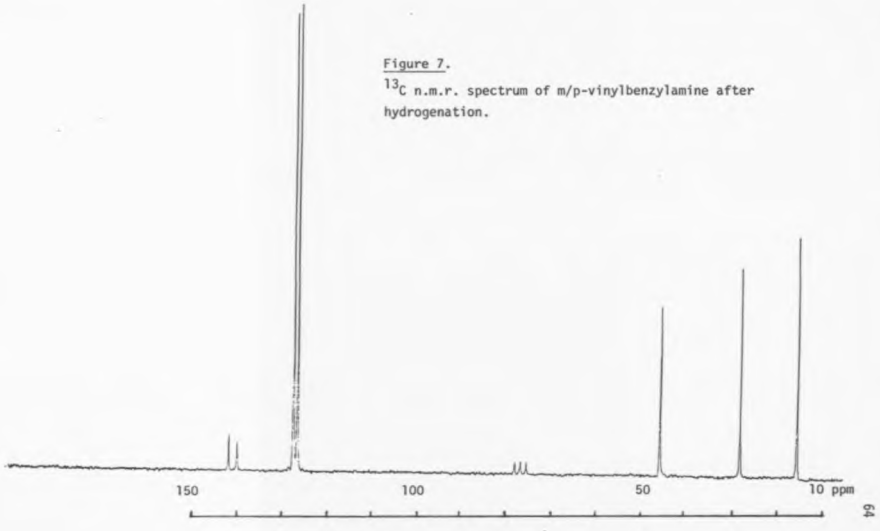
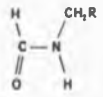


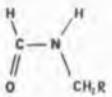
Figure 7.
^{13}C n.m.r. spectrum of m/p-vinylbenzylamine after hydrogenation.

Due to the hygroscopic nature of the p-vinylbenzylamine (10b) and its methiodide derivative, no satisfactory elemental analysis was obtained. Samples for n.m.r. spectroscopy could however be obtained by microdistillation from potassium hydroxide. The crude amine was sufficiently pure to be used in the next stage of the synthesis. The presence of the saturated impurity was not considered to be important (although it could be removed by careful recrystallization of the formamide (11b)) since it would not be included in the polymerized product.

The conversion of p-vinylbenzylamine (10b) to the formamide (11b) was carried out in good yield (76%) using ethyl formate. The n.m.r. spectrum of p-vinylbenzylformamide (11b) (figure 8) shows minor resonances at 4.21 ppm (CH_2) and 7.96 ppm (CHO) due to the second minor conformation possible for the formamide group. Due to the restricted rotation about the C-N bond, the formamide may be present in either cis (I) or trans (II) forms. The latter predominates[7].



I cis



II trans

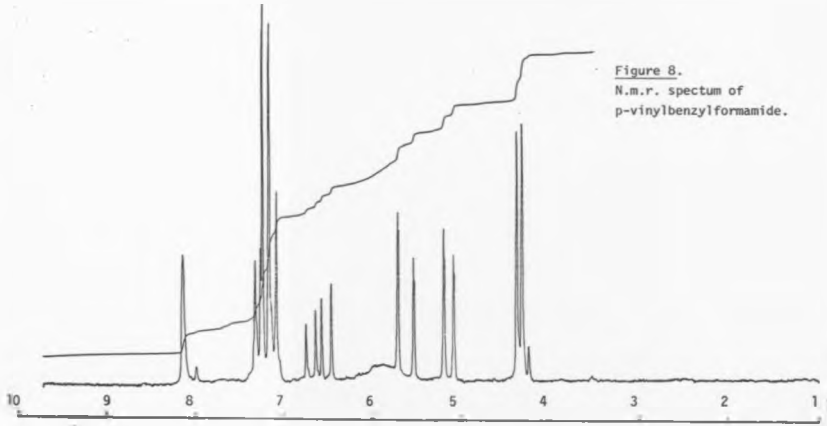


Figure 8.
N.m.r. spectum of
p-vinylbenzylformamide.

One of the reasons for loss of yield at all stages of the synthesis is the polymerizable nature of the vinyl group - causing some loss in each step, particularly at elevated temperature. The overall yield for the four-stage synthesis of p-vinylbenzylformamide from p-chlorostyrene is 29%).

(b) From m/p-chloromethylstyrene

The alternative route to vinylbenzylformamide, via chloromethylstyrene, yields products with a mixture of meta and para isomers due to the isomeric mixture in commercial chloromethylstyrene (60% meta, 40% para). Since this is unlikely to affect the eventual complexing properties of the polymer this was considered preferable to the multistage synthesis of pure p-chloromethylstyrene[8,9], in poor yield (~ 50%). The additional resonances due to the meta isomer can be clearly seen on the m/p-amine (10a) ^{1}H n.m.r. spectrum (figure 9) when compared to that of the p-amine (10b) (figure 4). m/p-Vinylbenzylphthalimide (2) was prepared from m/p-chloromethylstyrene and potassium phthalimide in dry dimethylformamide, and after recrystallization from chloroform/petroleum ether (85%) was converted to m/p-vinylbenzylamine (10a) using hydrazine hydrate in ethanol (42%). Again, some reduction of the vinyl group was seen, estimated from ^{1}H n.m.r. (figure 9) to be approximately 19%, a slightly higher proportion than that seen in the synthesis using lithium aluminium hydride to reduce p-vinylbenzamide (13%). In the case of the hydrazinolysis, the intermediate formed was presumed to be the amine salt of the phthalhydrazide (figure 10), (which is often isolated in hydrazinolysis of phthalimides)[10] and was converted to the amine by treatment with hydrochloric acid.

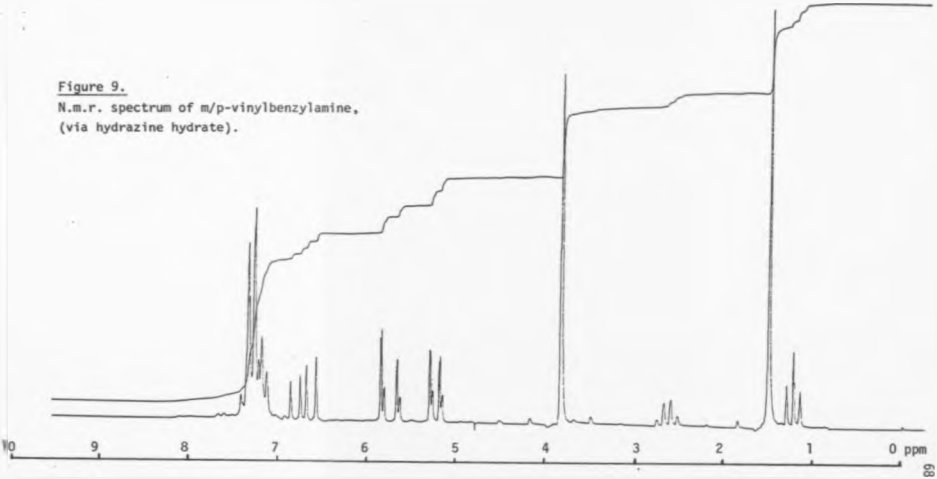


Figure 9.
N.m.r. spectrum of m/p-vinylbenzylamine,
(via hydrazine hydrate).

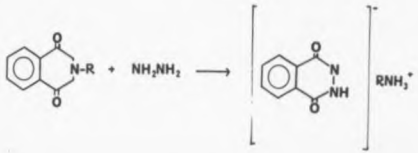


Figure 10, Formation of the phthalhydrazide

Conversion of m/p-vinylbenzylamine (10a) to m/p-vinylbenzylformamide (11b) was carried out in good yield by reaction with ethyl formate.

(2a) Polymerization and further modification of resins derived from p-vinylbenzylformamide (11b)

A small sample of p-vinylbenzylformamide (11b) was successfully homopolymerized using benzoyl peroxide as initiator, and exhibited a strong carbonyl stretching frequency at 1670 cm^{-1} (figure 11). A sample of the formamide (11b) was also successfully copolymerized with styrene and divinylbenzene in toluene solution to produce a polymer with a similar carbonyl stretching frequency, (figure 12). A sample of this latter polymer was dehydrated using p-toluenesulphonyl chloride and pyridine (see later) to yield the supported isocyanide (6), (figure 13).

Several attempts at suspension copolymerizations involving p-vinylbenzylformamide were made, as described in the experimental section. These polymers exhibited a much weaker infrared carbonyl stretching band at 1670 cm^{-1} together with a larger band at 1720 cm^{-1} (figure 14). The band at 1720 cm^{-1} was presumed to be caused by the presence of residual suspension stabilizer, poly(vinyl alcohol), which was not removed by the washing procedure. The alcohol is 88% hydrolysed from poly(vinyl acetate) and as such would have an infrared carbonyl stretching frequency around 1720 cm^{-1}.

These resins were successfully dehydrated using p-toluenesulphonyl chloride and pyridine to yield polymers exhibiting an isocyanide frequency at 2140 cm^{-1},(figure 15) but the isocyanide content, determined by titration with thiocyanic acid (see later for details, also experimental section) was only in the range 0.05 - 0.10 mmol g^{-1}. In contrast, the solution polymer produced by copolymerizing p-vinylbenzylformamide (11b) with styrene and divinylbenzene in toluene solution of dehydrated to yield a polymer with an isocyanide content of 0.3 mmol g^{-1}. Based on the titration figures and the weakness of the 1670 cm^{-1} band in the infrared spectrum, it was concluded that little or no formamide was actually incorporated into the resin produced. This may be traced to

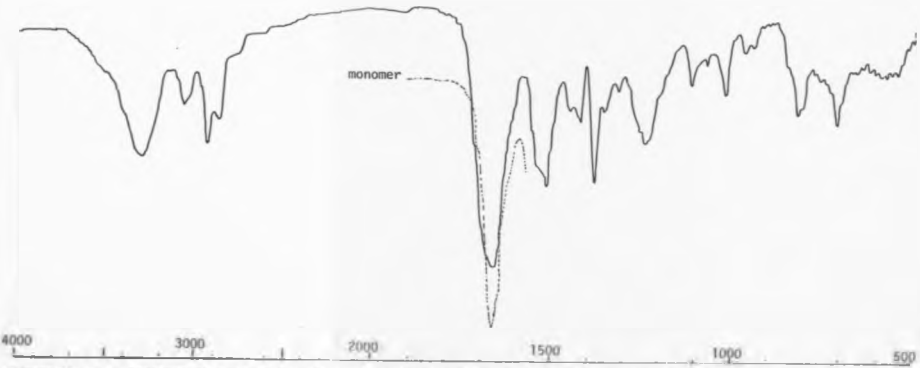


Figure 11. I.R. spectrum of product from homopolymerisation of p-vinylbenzylformamide, showing the position of the monomer ν_{CO}

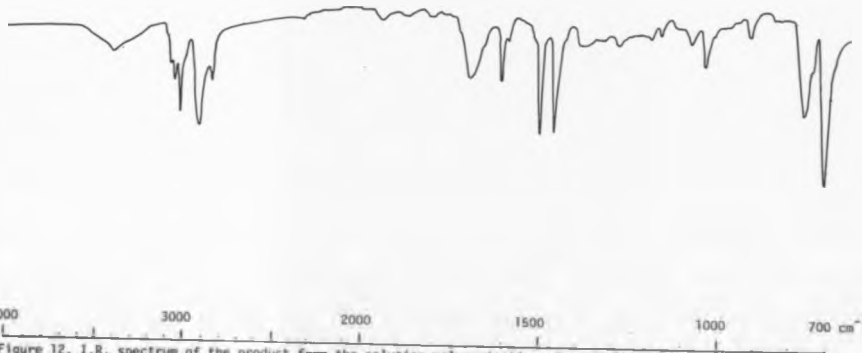


Figure 12. I.R. spectrum of the product from the solution polymerization of p-vinylbenzylformamide with styrene and divinylbenzene.

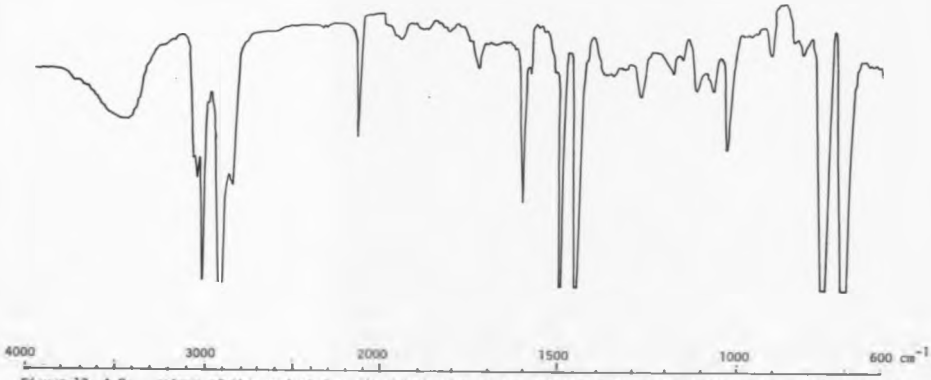


Figure 13. I.R. spectrum of the product from the dehydration of the solution polymer (p-vinylbenzylformamide, styrene and divinylbenzene).

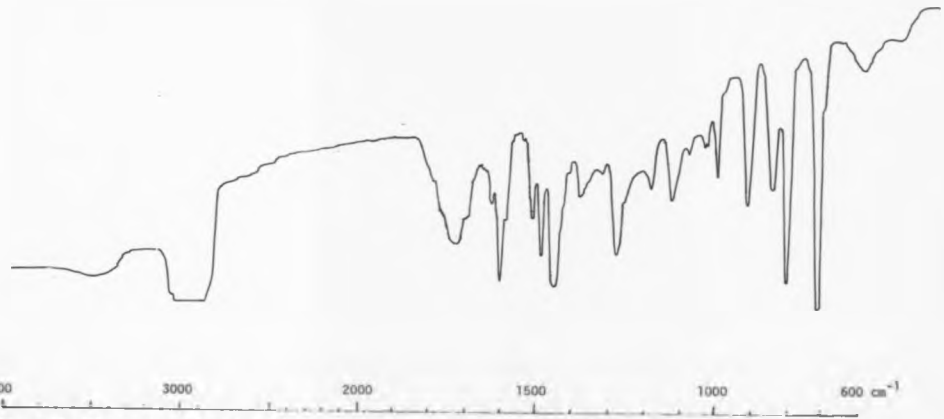


Figure 14. I.R. spectrum of product from suspension polymerisation of p-vinylbenzylformamide/styrene/divinylbenzene using PVA as suspension stabilizer.

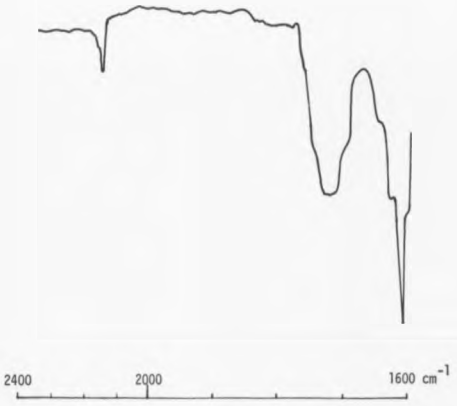


Figure 15.
I.R. spectrum of product from attempted dehydration of p-vinylbenzylformamide/styrene/divinylbenzene copolymer, (suspension polymerisation).

solubility; though the p-vinylbenzylformamide (11b) was found to be virtually insoluble in water at room temperature, it is seven times more soluble in water at 70 °C than in toluene (representing the organic layer). Thus, most of the formamide (11b) will remain in the aqueous layer (and will probably homopolymerize there). Some loss of functionalized monomer due to water solubility may be expected for polar molecules, and such results have been reported by Greig and Sherrington[11], for 4-vinylpyridine. However, in the case of the formamide (11b), the proportion of monomer which resides in the aqueous phase is so large that suspension polymerization of that monomer in water is not a realistic proposition.

One puzzling feature is that the incorporation of p-vinylbenzylformamide (11b) is calculated to be 0.3 - 0.6 mmol g^{-1}, based on the microanalysis figures for these suspension polymerization products, but the best conversion to isocyanide (6) obtained was only 0.12 mmol g^{-1} (determined by titration). Some incorporation of formamide (11b) would be expected as some of the monomer will remain in the organic layer. However, if all, or most of this small amount is incoporated towards the beginning of the polymerization, the formamide will then be concentrated in the highly crosslinked inaccesible regions of the polymer bead, and will not be available for dehydration, although it will be detected by microanalysis. In this case, it is expected that the infrared spectrum of the polymer would exhibit a strong carbonyl stretch at 1670 cm^{-1} but this is not seen. It is therefore assumed that little or no incorporation of the formamide into the suspension polymerization product takes place.

A possible explanation for the high % nitrogen microanalysis figures for these formamide resins is that the formamide (11b) is incorporated into the resin, but then most of it is hydrolysed to the amine by the presence of the water. This polymer product would have a high % nitrogen microanalysis figure, but only a small amount of isocyanide could be produced on dehydration (as only a small amount of formamide would remain

after hydrolysis). Due to the presence of the polymer backbone, it is not possible to distinguish any of the amine bands in its infrared spectrum, therefore if conversion to the amine did take place, this could not be confirmed. However, in a similar experiment using benzyl formamide dissolved in dichloromethane and stirred in water at 70 °C for 5 hours, then stirred at room temperature for 48 hours, no hydrolysis was observed. The n.m.r. and I.R. spectra of the benzyl formamide before and after the experiment are identical. (Figures 16 and 17).

It was hoped to produce polymers having a range of pore sizes in these suspension copolymerizations using p-vinylbenzylformamide (11b). This is carried out by varying the type and amount of diluent used (for details see table 2, experimental section) although the presence of the functionalized monomer will also have some effect. It was expected that those polymers prepared in the presence of heptane, a non-solvating diluent, would have larger pore sizes than those prepared in the presence of a solvating diluent (diethylbenzene). The exclusion limits quoted in table 1 (experimental section) are a measure of the actual size of the pores (see later in discussion), i.e. the bigger the exclusion limit, the larger the pore size. Since only a small proportion of the functionalized monomer was present in the organic phase during the polymerization, and this amount may well vary with time, or may not be evenly distributed throughout the organic layer, it is very difficult to draw any real conclusions from the results obtained when trying to produce resins of definite pore sizes. It can be seen however, that the presence of the formamide (11b) and the variation of the percentage of divinylbenzene and of diluent have a striking effect on the pore size of the resins produced. This will be discussed in more detail later, with respect to resins containing m/p-vinylbenzylphthalimide (3).

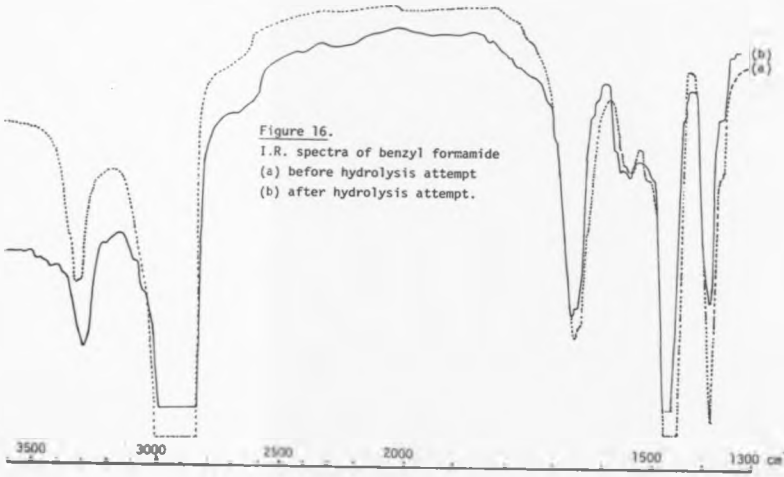


Figure 16.
I.R. spectra of benzyl formamide
(a) before hydrolysis attempt
(b) after hydrolysis attempt.

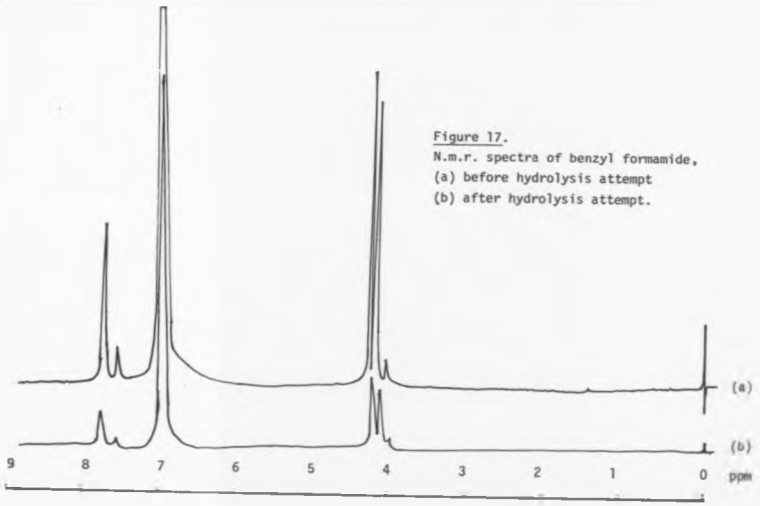


Figure 17.
N.m.r. spectra of benzyl formamide,
(a) before hydrolysis attempt
(b) after hydrolysis attempt.

Three low crosslinked gel-type resins were also prepared at Polymer Laboratories Ltd. (by the author). These resins were extremely difficult to filter and the product was eventually separated by centrifugation. This problem was most likely caused by a very small particle size for the beads and perhaps an excessive amount of suspension stabilizer. Calculated on the weight of monomers used, 10g, the amount of stabilizer recommended by Hodge and Sherrington[12] would be in the range 0.5g - 1.5g, although the amount used, 5g, was recommended by Polymer Laboratories Ltd. These resins also exhibited similar infrared spectra to those described earlier, (see figure 18, for example) and could not be effectively dehydrated. This is further confirmation of the low level of incorporation of the formamide (11b) as the low crosslinked resins will swell considerably in good solvents, thus leaving very little inaccessible matrix in which the formamide could be locked away to avoid dehydration.

(b) Polymerization and further modification of resins derived from m/p-vinylbenzylphthalimide (2)

Since the amine (10), amide (9) and acid (8) precursors of the formamide (11) (in the synthesis from p-chlorostyrene) might be expected to give similar problems due to water solubility, the monomer of the preceeding step in the alternative synthesis, (from m/p-chloromethylstyrene), the m/p-phthalimide (2) was examined as a potential candidate for suspension polymerization. The water solubility of the monomer (2) was found to be very low; 0.5g/l at 70°C. A homopolymerization was carried out to confirm that m/p-vinylbenzylphthalimide (2) was polymerizable, the polymer product having infrared carbonyl stretching frequencies at 1720(s) cm^{-1} and 1775(w) cm^{-1}, (figure 20) as does the monomer (figure 19).

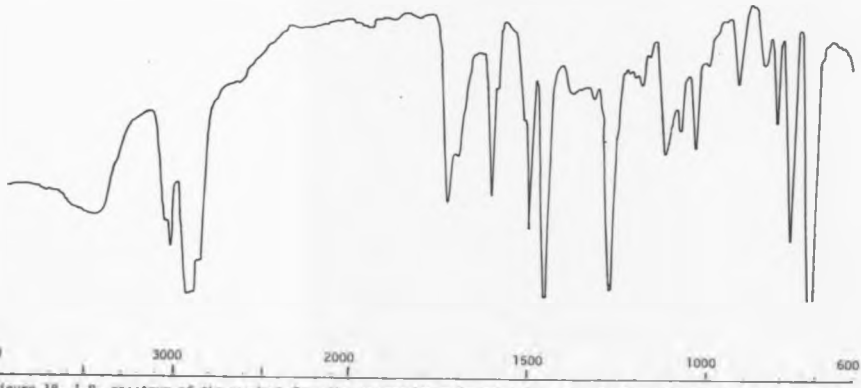


Figure 18. I.R. spectrum of the product from the suspension polymerization of p-vinylbenzylformamide with styrene and divinylbenzene, low crosslinked resin (JCPL22).

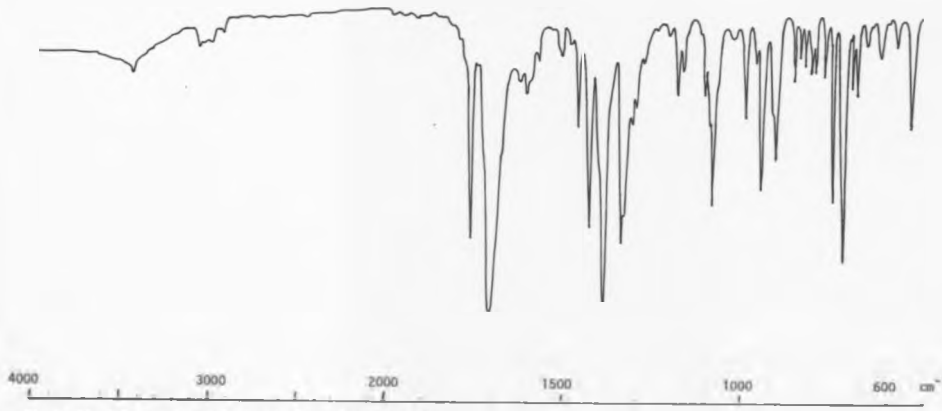


Figure 19. I.R. spectrum of m/p-vinylbenzylphthalimide.

Figure 20. I.R. spectrum of the product from the homopolymerization of m/p-vinylbenzylphthalimide.

The m/p-phthalimide monomer was also copolymerized with styrene and divinylbenzene, in toluene solution, to yield an appropriately functionalized polymer which also had infrared carbonyl stretching frequencies at 1720(s) and 1775(w) cm^{-1}, (figure 21). The monomer was then used in suspension polymerizations, with styrene and divinylbenzene. Copoly(styrene-maleic anhydride) was used as the suspension stabilizer as it was found to be more easily washed out of the resin after polymerization.

The resins produced can be described as two types - gel-type or macroporous. In the work described here gel-type refers to a resin of low divinylbenzene content, polymerized in the absence of diluent, in contrast to macroporous resins of high divinylbenzene content, polymerized with a diluent present. It is possible to make resins using a combination of these factors, i.e. low divinylbenzene content, with a diluent present, or high divinylbenzene content, without a diluent present. The diluent may also be of two types - solvating, non-solvating or a mixture of both. Thus complex systems can be built up by the many combinations of these variables.

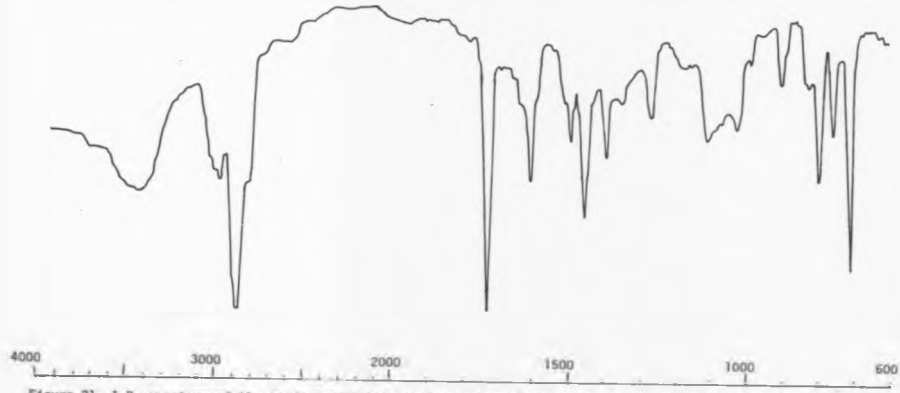


Figure 21. I.R. spectrum of the product from the solution polymerization of m/p-vinylbenzylphthalimide with styrene and divinylbenzene.

The production of macroporous beads is a function of the percentage of divinylbenzene and the percentage of diluent (the latter calculated as a weight % of the total amount of monomer and diluent), and it is these two variables which determine whether a gel-type or macroporous resin is produced. A graph can be drawn of % divinylbenzene against diluent which will determine the so-called macroporous domain for a particular resin i.e. the area on the graph in which the proportions of divinylbenzene and diluent correspond to a macroporous resin. The position of the macroporous domain will vary for different diluents, and a large difference is seen between the domains of solvating and non-solvating diluents. Figures 22 and 23 show such graphs for a simple sytrene/divinylbenzene system.

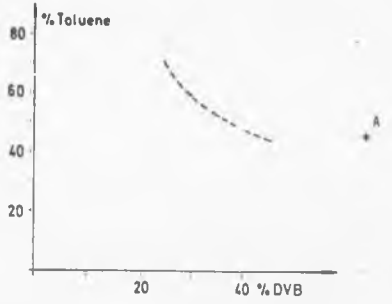
Exactly what happens on the border and outside the macroporous domain is not well understood. Guyot[13] et al state that further work on this area is necessary, but list the following as common features of the lower domain:

- very small surface area
- no pore volume

It is presumed that the resin JCPL9 (referred to in section 2(a) and table 2 in experimental section) which was prepared by the suspension polymerization of p-vinylbenzylformamide with divinylbenzene, using heptane as diluent, falls into this category i.e. is outside the macroporous domain, as gel permeation chromatography results showed no pores present.

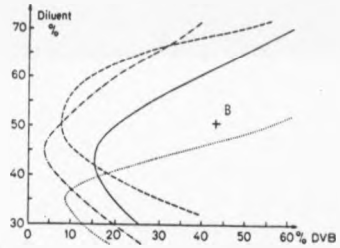
Using Guyot's method and his diagrams for styrene/divinylbenzene, calculations for the two macroporous phthalimide resins prepared indicate both resins should be truly macroporous as both points fall inside the appropriate macroporous domains.(Points A and B on figures 22 and 23) Guyot[14] states that replacement of styrene by chloromethylstyrene in the monomer mix has little effect on the position of the macroporous domain,

Figure 22.



Position of the macroporous domain for toluene as diluent.

Figure 23.



Position of the macroporous domain for various diluents; - - - benzyl alcohol, - · - · - ethyl hexanoic acid, —— heptane, · · · · · pentanol.

although chloromethylstyrene is a more reactive monomer. The intention was to prepare two resins of different pore sizes - the one prepared with toluene as diluent (i.e. solvating diluent) should have a relatively small pore size and the other resin, with heptane/diethylbenzene, would be predominately non-solvating, and so have a large pore size. However both resins have a similar exclusion limit (~ 700, molecular weight of polysytrene) see figures 24a and 24b indicating a pore size of approximately 50Å. There are two possible explanations for this:

(i) The effect of the inclusion of 10% diethylbenzene - added to keep the phthalimide in solution - may be very significant. Although the divinylbenzene/diluent combination falls well within the macroporous domain on the graph for a simple styrene/divinylbenzene system with heptane as diluent, (point B figure 23) the effect of the relatively small amount of diethylbenzene may have a significant effect. A similar effect has been observed[15] using mixtures of solvating and non-solvating diluents in polymerization mixtures containing 30% styrene, 10% divinylbenzene and 60% diluent. Heitz[15] states that good solvents, such as toluene and diethylbenzene, produce resins (for the above reactants) with exclusion limits of approximately 10,000 (molecular weight of polystyrene - explanation see later). He found that altering the diluent composition by addition of a non-solvating diluent which was more polar than the growing polymer resulted in a steady increase in pore size, as expected. However, using a non-polar non-solvent, such as a hydrocarbon (e.g. heptane), the exclusion limit decreased drastically, for only a small change in composition. It is therefore assumed that this is the effect seen for the phthalimide-styrene-divinylbenzene polymer produced with heptane/diethylbenzene as diluent.

Figure 24a.
Determination of the exclusion limit for polymer JC220.
(m/p-Vinylbenzylphthalimide/styrene/divinylbenzene copolymer,
52% crosslinked, toluene as diluent).

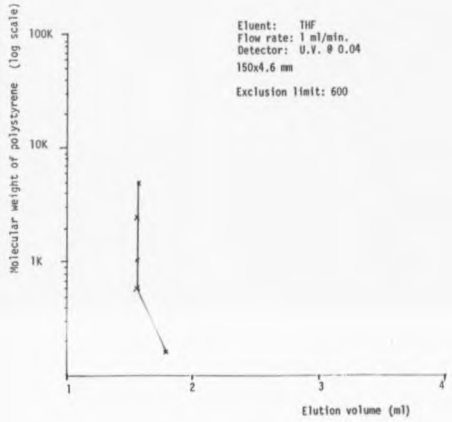
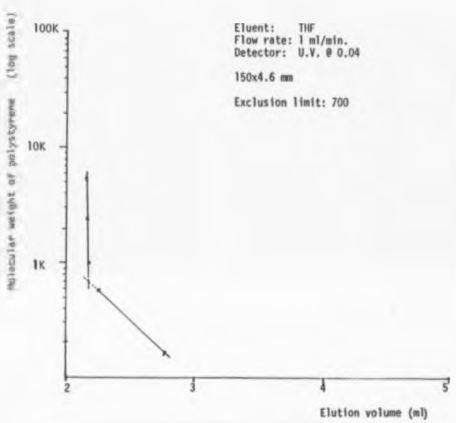


Figure 24b.
Determination of the exclusion limit for polymer JC107.
(m/p-Vinylbenzylphthalimide/styrene/divinylbenzene copolymer,
52% crosslinked, heptane/diethylbenzene as diluent).



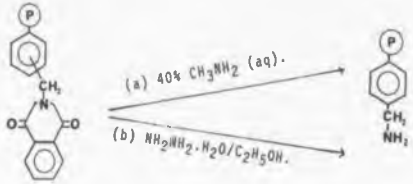
(ii) Alternatively, or in addition to the above, the effect of the functionalized monomer (phthalimide (2)) may be responsible for the movement of the point on the graph to an area (close to the boundary, presumably) of small pore size within the macroporous domain. A considerable amount of further work would therefore be necessary before resins of a particular pore size could be produced.

The pore size determinations were carried out at Polymer Laboratories Ltd., and were the exclusion limits found by g.p.c. (gel permeation chromatography) analysis of the resins. In this technique, the resin is pressure packed into a stainless steel (h.p.l.c. type) column, and polystyrene standards of known molecular weight are injected down the column, in a standard g.p.c./h.p.l.c. set up. The time taken for these standards to be eluted is measured, the standards which are small enough to enter the resin pores taking longer to pass through. Those standards which have molecular size too large to enter the pores are eluted straight through the column quickly. A graph of elution volume (corresponding to time) against the log of the molecular weight of the polystyrene standards shows a sharp cut-off point at which the standards are too large to enter the pores (see figures 24a and 24b for example). This is known as the exclusion limit, and can be correlated to a particular pore diameter.

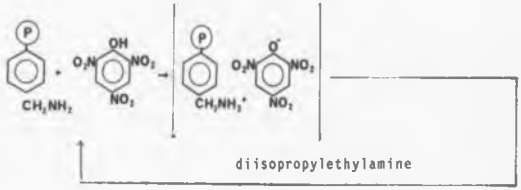
As a result of these uncertainties, further synthetic and complexation studies were limited to gel-type resins. Such resins usually have a low divinylbenzene content, often as low as 1 or 2%. The resins prepared for this work were generally 9% crosslinked, although 2% crosslinked samples have also been prepared. Unless otherwise stated, the resins referred to in the remainder of this thesis are 9% crosslinked.

The nitrogen microanalysis figures for the resins (3) prepared by benzoyl peroxide initiated suspension polymerization of m/p-vinylbenzylphthalimide, styrene and divinylbenzene, consistently indicate a level of phthalimide monomer (2) incorporation which is considerably higher than the proportion present in the polymerization mix. It is therefore concluded that the phthalimide monomer is more reactive relative to styrene and the ethylstyrenes present. Therefore some proportion of the styrene and ethylstyrenes may homopolymerize (or not polymerize at all) and will be washed out of the resin. This is consistent with results found by Bartholin et al[16] who state that "the whole ethylvinylbenzene (ethylstyrene) is not consumed during polymerization". A higher percentage of phthalimide incorporation is seen for the 2% crosslinked resin, (relative to 9%) although the same percentage of monomer is included in the monomer mix. This is consistent with the suggestion that the phthalimide is more reactive than styrene, since as one reduces the divinylbenzene content (divinylbenzene is assumed to be the most reactive monomer present) the next fastest monomer (phthalimide) will tend to be incorporated in a seemingly greater proportion.

The 9% crosslinked polymer-supported phthalimide was converted to the supported amine by two methods, using either methylamine or hydrazine hydrate. The latter was preferred, and was used in all subsequent batches, since although the yield of amine (determined from the reaction with picric acid) was only slightly better, the reaction was easier to perform on a large scale.



The concentration of amine functionality in the resin was determined by the method of B.F. Gisin.[17]



This picrate determination has an error of $\pm$ 0.15 mmol g^{-1} determined by a blank experiment using an unfunctionalized styrene/divinylbenzene resin. Some colour is taken up by the resin regardless of its amine content, and some very slight residual colour remains after repeated washings. Duplicate determinations on samples from the same batch of resin gave values within the error range, so in most cases duplicate determinations were not carried out. From Table 3 (experimental section, section 5.3.) it is seen that in most cases the actual amine content by picrate determination is less than the content calculated for 100% yield. (This calculation takes into account the weight loss experienced by the polymer in the phthalimide (3) to amine (4) transformation.) In the case of resins JC205 and the first set of analyses

for JC213, it is necessary to consider the errors involved in the analyses for these to be less than 100% yields. The error limits are calculated by considering the error in the microanalysis ($\pm$ 0.3% on the actual % N figure i.e. ~ 0.2 mmol g^{-1} calculated for each individual N figure) and also the error in the picrate determination (found to be ~ 0.2 mmol g^{-1} by blank titration.) It can be seen that the two ranges for the actual picrate determination and the calculated figure for amine content overlap in all cases.

An example of the calculations for JC205 is given below:

(1) phthalimide content (from microanalysis):
mol wt phthalimide 263, mol wt amine 133.

$\therefore$ wt loss (for 1g) = 1.08 (133) = 143.64 mg

1-0.1436g = 0.8564g

$\frac{1.08 \text{ mmol}}{0.8564\text{g}}$ = 1.26 mmolg^{-1} expected amine content

Error in microanalysis $\pm$ 0.2 mmol g^{-1}

$\therefore$ expected amine content = $\underline{1.06 - 1.46 \text{ mmol } g^{-1}}$

Amine content from picrate determination: 1.43 mmol g^{-1}

Error in picrate determination $\pm$ 0.2 mmolg^{-1}

$\therefore$ Amine content from picrate determination = $\underline{1.23 - 1.63 \text{ mmol } g^{-1}}$

Note the two ranges overlap.

In the case of the macroporous 52% crosslinked phthalimide functionalized resin JC107, two samples were analysed and gave widely differing results, calculated as 1.96 and 0.59 mmol g^{-1}. The analysis figures for the amine derived from this resin also gave inconsistent results. The %N figures for the amine were: zero, zero; 1.24, 1.17, 1.91, 1.52. Two picrate determination were carried out giving results of 0.63 and 0.49 mmol g^{-1}, which are just inside the error limits for the technique ($\pm$ 0.15 mmol g^{-1}). However duplicate results were usually much closer, i.e. 1.31 and 1.24 mmol g^{-1} for one batch of 9% crosslinked polymer supported amine (4).

Note Microanalysis figures are not usually quoted for the amine resins as any residual phthalimide present will affect the %N figure. However these values are included to illustrate the widely differing results obtained for this resin.

From these results, it is evident that this macroporous 52% crosslinked resin does not have a uniform distribution of functionality. This is in contrast to results obtained by Greig and Sherrington[11], and by Grubbs and Sweet[18], who in independent experiments found a uniform distribution of the required functionality. Grubbs and Sweet modified preformed polystyrene beads by chloromethylation and phosphination followed by reaction with Rh(I) complexes. They found, by microprobe analysis, that a uniform distribution of rhodium was achieved when using an excess of the rhodium complex. Sherrington and Greig included 4-vinylpyridine in the monomer mix with styrene and divinylbenzene, and reacted the resin beads produced with 1-iodooctadecane. Microtomed sections of both 5% and 37% crosslinked beads (nominal crosslink ratio) showed the charactersistic pyridinium iodide charge transfer colour across the whole of their surface. The macroporous 52% crosslinked phthalimide resin (3), JC107, was prepared in the presence of a mixture of heptane and diethylbenzene (9:1). The diethylbenzene was necessary to keep the m/p-phthalimide monomer (2) in

solution, and so perhaps it is some aspect of this non-compatability of the monomer and diluent which causes the non-uniform distribution of monomer throughout the polymer beads. This may also have some affect on the macroporous domain for the system used, and may therefore also be partly responsible for the small pore size produced.

The conversion of the polymer-supported phthalimide (3) (figure 25) to the amine (4) is accompanied by the decrease or disappearance of the infrared band at 1720 cm^{-1} of the phthalimide (the band at 1775 cm^{-1} disappears), but the bands associated with the amine itself (N-H bending, C-N stretching etc) are not clearly seen as they are all hidden by those of the polymer backbone, (figure 26). In all the potassium bromide disc samples made, an infrared band at $\sim$ 3300 cm^{-1} is visible and it is this which hides the amine N-H stretching band. It seems most likely that this is due to moisture absorbed by the potassium bromide during the sample preparation.

With the conversion of the supported amine (4) to the formamide (5) using ethyl formate, the appearance of a new strong carbonyl stretching vibration at 1670 cm^{-1} is observed in the infrared spectrum, (figure 27). This reaction is assumed to go in very good yield, since the major factor responsible for less than 100% yields in the monomer synthesis involved loss of a small amount of polymerized material.

Several methods were examined for the dehydration of the supported formamide (5) to the isocyanide (6):

(a) p-toluenesulphonyl chloride and pyridine;

$$R - NHCHO + CH_3C_6H_4SO_2Cl + 2\ C_5H_5N \longrightarrow R - N \equiv C + [C_5H_5NH]^+[CH_3C_6H_4SO_3]^- + [C_5H_5NH]^+Cl^-$$

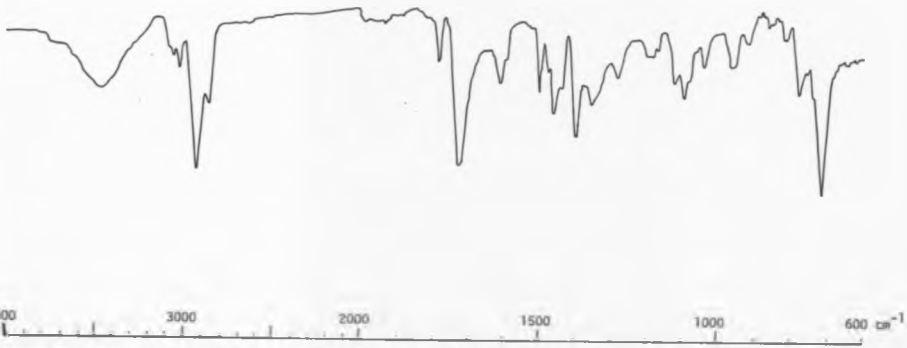


Figure 25. I.R.spectrum of the product from the suspension polymerization of m/p-vinylbenzylphthalimide with styrene and divinylbenzene.

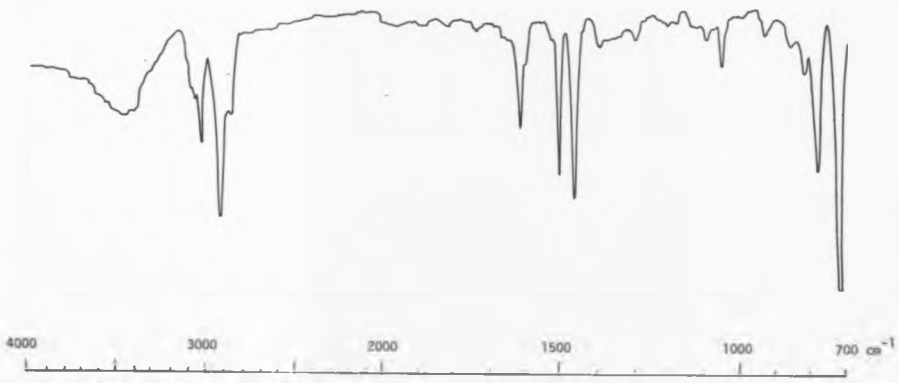


Figure 26. I.R. spectrum of the polymer-supported amine.

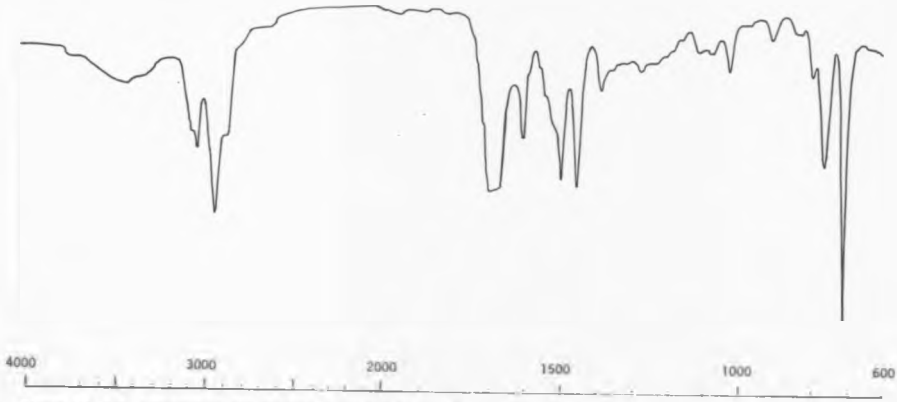


Figure 27. I.R. spectrum of the polymer-supported formamide.

(b) diphosgene and triethylamine;

$$2R\text{-}NHCHO + ClCOOCCl_3 + 4NEt_3 \longrightarrow$$

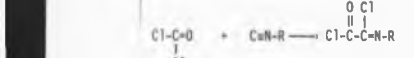
$$2R\text{-}N{\equiv}C + 2CO_2 + 4NEt_3.HCl$$

(c) phosgene and triethylamine;

$$R\text{-}NHCHO + COCl_2 + 2NEt_3 \longrightarrow$$

$$R\text{-}N{\equiv}C + CO_2 + 2NEt_3.HCl$$

Of these, the only method which gave consistently good results was method (a). No conversion to the isocyanide (b) was observed using diphosgene, although several variations of method were attempted. The problems encountered with phosgene were due to the difficulty of delivering an exact amount of very toxic gas. If too little is used the reaction does not go to completion - as evidenced by a strong residual carbonyl absorption due to the formamide (5) at 1670 cm^{-1}, in addition to the isocyanide absorption at 2140 cm^{-1} in the infrared spectrum (figure 28a). If an excess of phosgene is used, the resulting polymer shows neither a formamide carbonyl stretching frequency, nor an isocyanide CN stretching frequency. However, a very broad band is seen at 1700-1800 cm^{-1} (figure 28b) which may possibly be assigned to a product arising from further reaction of the isocyanide(6) with phosgene. A possible equation is given below, based on the reaction of isocyanide with acetyl chloride.[4]



The product shown may then react with a further molecule of isocyanide to produce oligomers of the type;

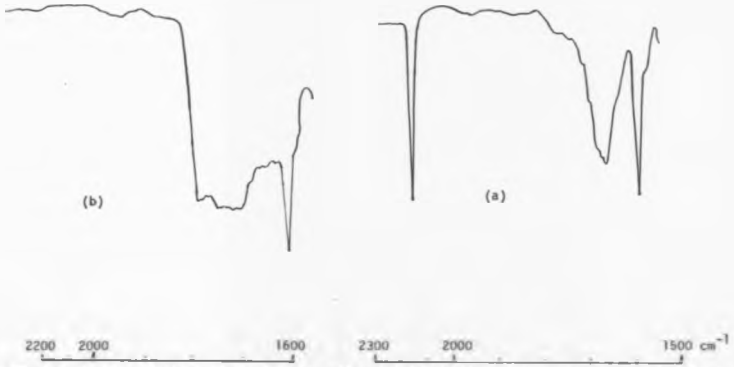


Figure 28. I.R. spectra of the products from the attempted dehydration of the polymer-supported formamide using (b) excess phosgene, or (a) 1 equiv. phosgene.

however such further reaction may not be possible on a polymer support. A product of this nature would be expected to have both carbonyl and CN stretching frequencies in the region of 1700 cm^{-1} in the infrared spectrum.

The isocyanide content of the resin was determined by the titration method of Arora, von Hinrichs and Ugi.[19]

a triazinedithione

An alternative method of determining the isocyanide content of resins involving bromination has recently been reported.[20] This method is found to be more satisfactory for higher loadings of isocyanide (up to 3 mmol g^{-1}) but for polymers with low degrees of substitution, the method gave similar results to the thiocyanic acid method.

Using p-toluenesulphonyl chloride and pyridine, conversion of approximately 0.6 mmol g^{-1} (~50% conversion, based on amine content of resin (4), as the reaction of the amine with ethyl formate is carried out in good yield). This may be improved to 0.8-1.0 mmol g^{-1} (61-77% conversion) by increasing the amount of pyridine present to ensure the absence of any acid in the dehydration mixture which may catalyse the polymerization of the isocyanide group[4]. It is probable that the reduced isocyanide level is caused by the polymerization of the isocyanide group, as the white formamide resin becomes light yellow-brown after dehydration. A small amount of aniline was also added to the reagents used in the dehydration as it is claimed that this helps to suppress polymerization[21]. The presence of a small, broad band at 1690-1730 cm^{-1} in the infrared spectrum (figure 29) may indicate the formation of some polymerized isocyanide containing a $>C{=}N-$ group. From the infrared spectrum there apears to be little or no unreacted formamide (5) present. A summary of the synthesis used for the gel-type resins is shown in figure 30.

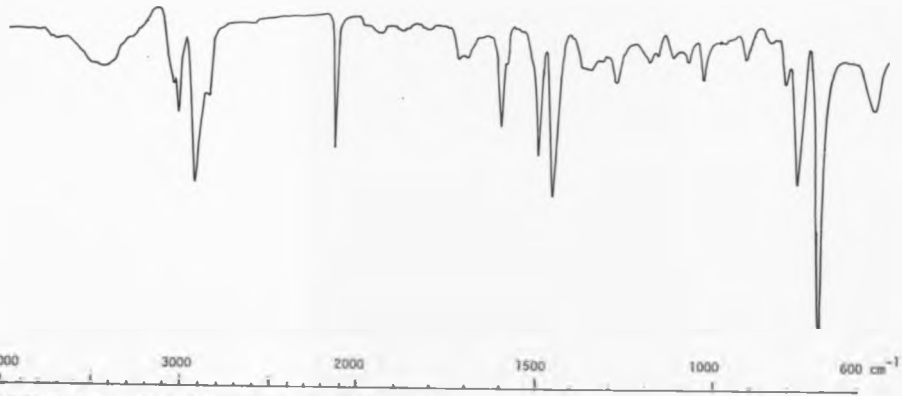


Figure 29. I.R. spectrum of the polymer-supported isocyanide.

It will be noticed that microanalysis, (C,H,N) values are only used to calculate the level of incorporation of the phthalimide monomer (2) into the resin (3) since only the nitrogen figure is useful, and all subsequent reaction products contain nitrogen. Each successive step will contain a proportion of nitrogen belonging to unreacted starting material (or by-product); thus, the nitrogen microanalysis for each step is not an accurate representation of the amount of new functionality present.

An attempt was made to produce a soluble homopolymer of p-vinylbenzylformamide (11b) by carrying out the homopolymerization on a large scale (10 g) but only a small amount (approximately 0.25 g) of the resulting polymer was found to be soluble in dichloromethane. It was hoped that a soluble isocyanide polymer could be prepared which could then be used in complexing experiments to produce a truly homogeneous isocyanide metal complex for use in catalytic studies. In view of the poor yield of soluble polymer, it was decided not to pursue this work further. However, the production of such soluble polymer supported isocyanide-metal complexes provides an interesting area for further work.

3. Polymerizations using allylformamide

An investigation was carried out to determine the feasibility of using allylformamide as a monomer in polymerizations with styrene/divinylbenzene, acrylic acid and methacrylic acid, leading to the synthesis of a supported isocyanide. Allylformamide is easily prepared from allylamine and ethyl formate in good yield.

$$\underset{(12)}{CH_2{=}CH{-}CH_2NH_2} + HCO_2C_2H_5 \longrightarrow \underset{(13)}{CH_2{=}CH{-}CH_2NHCHO} + C_2H_5OH$$

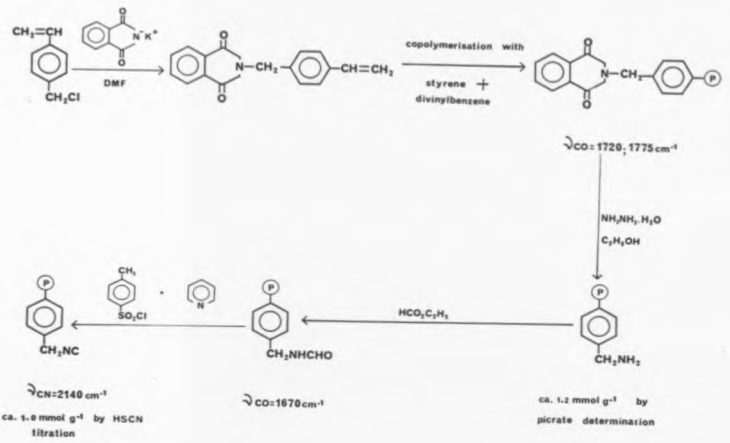


Figure 30. General scheme for the synthesis of the polymer-supported isocyanide, gel-type resins (9% & 2% crosslinked).

Homopolymerization and copolymerization of allylformamide (13) with acrylic or methacrylic acid has been reported.[22] Shcherbina et al state that allylamine (12) and allylformamide (13) will not homopolymerize using benzoyl peroxide as the free radical initiator. In the copolymerizations with acrylic or methacrylic acid, they achieved good yields only for mixtures with an (initial) predominance of the acid component. In keeping with this result, the rate of polymerization is fast at the start, but rapidly declines as the acid is used up. These copolymerizations were initiated with azobisisobutyronitrile (azbn).

Test-tube polymerizations were carried out using azbn or benzoyl peroxide, with various mixtures of styrene, divinylbenzene and allylformamide (13). Any allylformamide which appeared to have been incorporated was removed on Soxhlet extraction. A carbonyl stretching frequency at 1700 cm^{-1} was seen on the infrared spectrum of the polymer product (figure 31), but this disappeared after Soxhlet extraction with dichloromethane (figure 32). Benzoyl peroxide was preferred as the initiator, as the reaction with azbn was extremely exothermic and did not provide better results. It is therefore assumed that the reactivity of allylformamide (13) is too low for combination.

Copolymers of allylformamide with acrylic acid or methacrylic acid were then attempted. Some allylformamide appeared to be incorporated, as although the microanalysis figure for nitrogen decreases from 3.34 mmol g^{-1} to 2.68 mmol g^{-1} after Soxhlet extraction, there is still some nitrogen present. It is difficult to see the carbonyl stretching frequency of the allylformamide in the methacrylic acid (or acrylic acid) copolymers (figure 33) since it is partially hidden by the carbonyl stretching frequency of the acid itself, (figure 34, methacrylic acid only). Attempts to dehydrate these samples did not yield any isocyanide.

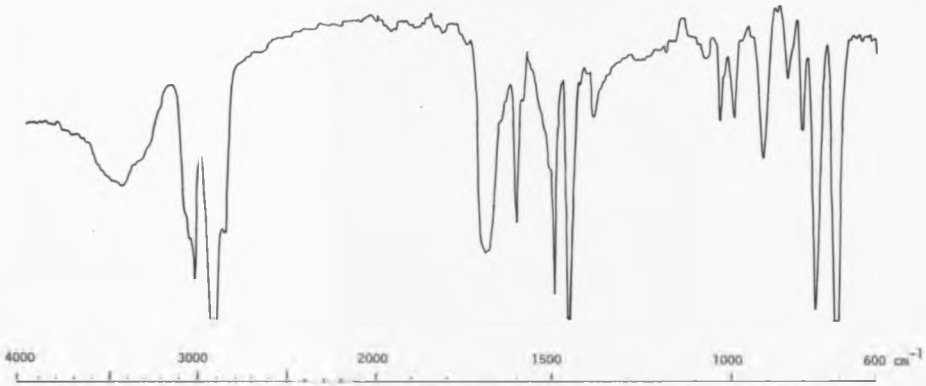


Figure 31. I.R. spectrum of the product from the copolymerization of allylformamide with styrene and divinylbenzene before Soxhlet extraction.

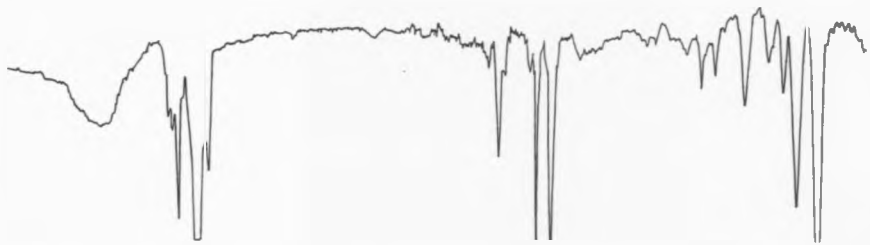


Figure 32. I.R. spectrum of the product from the copolymerization of allylformamide with styrene and divinylbenzene after Soxhlet extraction.

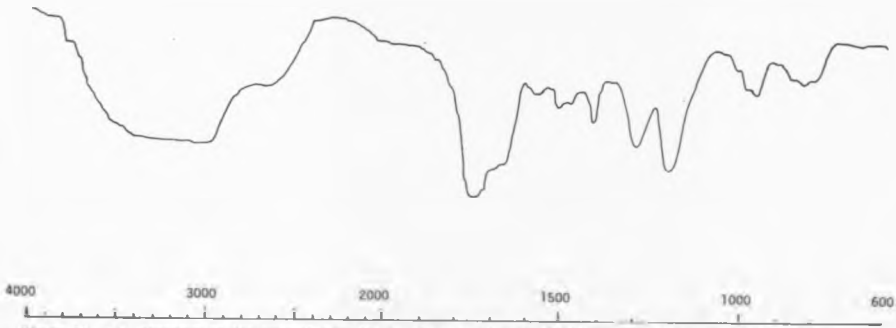


Figure 33. I.R. spectrum of the product from the copolymerization of allylformamide with methacrylic acid.

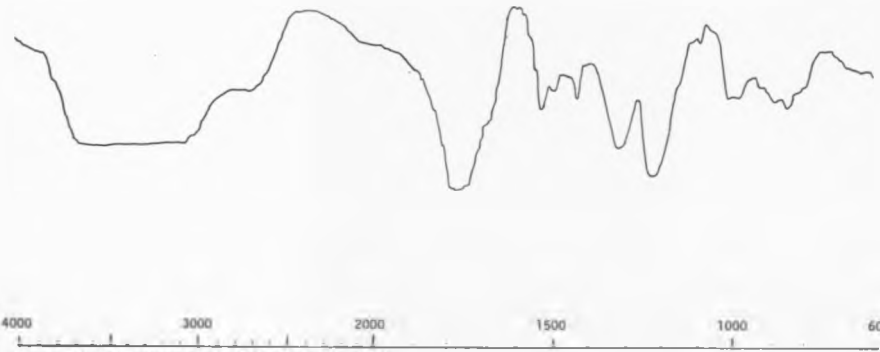


Figure 34. I.R. spectrum of poly(methacrylic acid).

Allyl compounds are known to be difficult to polymerize and indeed some allyl compounds have been used as inhibitors for other polymerizations, for example, allyl alcohol inhibits the polymerization of butadiene.[23] In view of the lack of reactivity of allylformamide (13), this work was not pursued further.

2.3 EXPERIMENTAL

N.m.r. spectra were recorded on either a JEOL FX-100 n.m.r spectrometer, or a Hitachi Perkin-Elmer R24B n.m.r spectrometer.

Infrared spectra were recorded on a Pye Unicam SP2000 spectrometer.

Ultraviolet spectra were recorded on a Varian DMS 100 spectrometer.

Gas chromatographs were run on a Pye Unicam 104 gas chromatograph. (For column details see appropriate section).

H.p.l.c and g.p.c data were recorded at Polymer Laboratories on Knauer equipment: h.p.l.c pump 64, U.V. photometer, differential refractometer or conductivity detector.

Metal, phosphorus and chlorine analyses were performed by the Microanalytical Laboratory, University of Manchester.

(A) Synthesis of the monomer, p-vinylbenzylformamide (11b)

1.1 Synthesis of p-chlorostyrene(7)

p-Chlorophenylmethylcarbinol was synthesized from 1,4-dichlorobenzene according to the procedure of Leebrick and Ramsden;[5] yield 64%, b.p. 110-120 °C at 3 mm Hg, and was dehydrated by means of the procedure of Overberger and Saunders,[24] to yield 41% p-chlorostyrene b.p. 52 °C at 2 mm Hg. Alternatively, the p-chlorostyrene (7) was purchased commercially.

1.2 Synthesis of p-vinylbenoic acid (8)

All glassware was flamed to remove moisture before any reagents were added.

A 500ml 3-necked flask was maintained under a dry nitrogen atmosphere. The flask was equipped with a mechanical stirrer, a 500 ml pressure-equalized dropping funnel containing p-chlorostyrene (7)(40 g,0.27 mol) in THF (150 ml, dry, distilled off sodium wire and benzophenone), a swan-necked adaptor holding a thermometer and a double surface condenser with a calcium chloride drying tube. Magnesium turnings (14 g,0.57 mol) were added to the flask, and ethyl bromide (5 ml) in THF (25 ml, dry, distilled off sodium wire and benzophenone) was added to activate the metal. When the temperature had fallen to below 60 °C the addition of the p-chlorostyrene in THF began. The rate of addition was such that the temperature was kept below 60 °C. (A bath of acetone-liquid N_2 was used to cool the reaction flask if the temperature increased above 60 °C). After the addition was complete (approx. 1 hour) , the reaction mixture was heated to 60 °C on an oil bath, for 15-20 minutes, followed by stirring for a further 60 minutes.

Dry carbon dioxide was bubbled into the reaction mixture for 2 hours, maintaining the temperature at approx. 40 ^{o}C by the use of an acetone/liquid N_2 bath. While still cooling the flask, distilled water was added until the excess Grignard reagent had all been neutralized - producing a large amount of gelatinous grey-white precipitate. The precipitate was filtered and treated as follows. The filtrate was worked up in a similar manner to that described in the literature (see next paragraph). The precipitate was treated with 2M NaOH and centrifuged. The supernatant liquid was decanted off and then filtered to remove any residual precipitate. It was then acidified with dilute H_2SO_4 to precipitate the product (4) which was filtered and dried at 30 ^{o}C in a vacuum oven. This procedure was repeated on the precipitate until no further p-vinylbenzoic acid was obtained. Yield 38.1g.

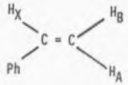
The "reaction mixture" filtrate was treated with CH_2Cl_2 and distilled water to produce two layers. The organic layer was separated, and the aqueous layer extracted twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and removal of the solvent gave 0.7 g product (4) when dry.

The product was spectroscopically pure and was used without further purification. (Total "crude" yield 38.8 g, 91%), m.p. 138-140 ^{o}C

Modifications of the literature method which were attempted, and were not found to be beneficial include (i) addition of dry ice to the reaction mixture, rather than pouring the latter onto dry ice and (ii) use of a saturated NH_4Cl solution to neutralize the excess Grignard while keeping the reaction mixture basic - in order to attempt to keep the product in solution.

All N.m.r. chemical shifts are recorded in ppm relative to TMS.

^{1}H N.m.r. (CDCl3): figure 35



9.3(s,br) COOH

7.43-8.06(m) Ph

6.76(d,d) H_X

5.86(d,d) H_A

5.39(d,d) H_B

J_{AX}=17.2 Hz

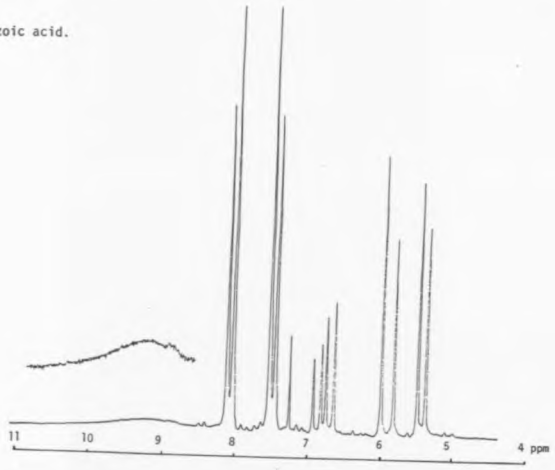
J_{BX}=10.9 Hz

J_{AB}= 0.9 Hz

I.R (Nujol mull): figure 36

cm^{-1}	
710	C=C out of plane (OOP)
858	C-H OOP p-disubstituted aromatic
908	C-H OOP monosubstituted vinyl
988	C-H OOP monosubstituted vinyl
1293	C-O str
1430	C-H scissor vinyl
1465	C=C aromatic
1610	C=C vinyl
1695(s)	C=O str
2850(br)	nujol (C-H str)
2920	nujol (C-H str)
3070(br)	OH str

Figure 35.
N.m.r. spectrum of p-vinylbenzoic acid.



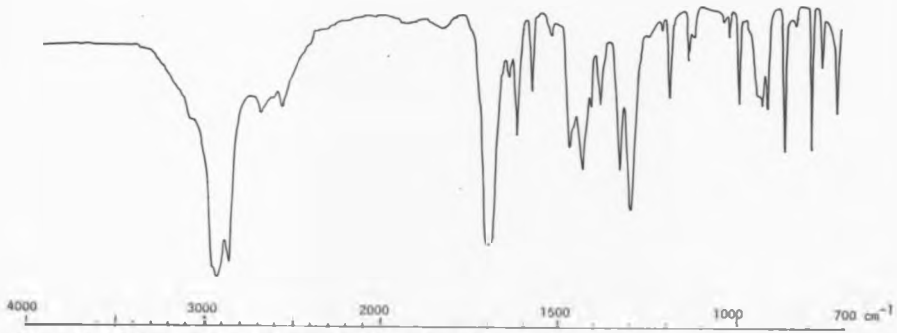


Figure 36. I.R. spectrum of p-vinylbenzoic acid, (nujol mull).

1.3 Synthesis of p-vinylbenzamide (9)

p-Vinylbenzoic acid (8)(7 g,0.05 mol) was placed in a 100 ml round bottomed flask fitted with a silica gel drying tube. Thionyl chloride (freshly distilled, 25 ml, 0.34 mol, -large excess required to thoroughly wet the acid) was slowly added. The mixture was stirred for 2 days, then filtered through celite on a glass sinter to remove any unreacted acid. The excess thionyl chloride was removed under reduced pressure. Anhydrous liquid ammonia was condensed into a 250 ml round bottomed flask and the acid chloride was added dropwise. After the residual ammonia had evaporated, the crude yield of dried products, p-vinylbenzamide (9) and ammonium chloride was 7.65 g (maximum 8.43 g). This mixture was used in the next stage of the synthesis without further purification. Yield (assuming amide and ammonium chloride are lost in equal proportions) 73%.

Amide

^{1}H N.m.r. ($CDCl_3$): figure 37

7.32-7.81(m)Ph

6.73 (d,d) H_X

5.90 (s,br) $CONH_2$

5.81 (d,d) H_A

5.34 (d,d) H_B

Acid chloride.

^{1}H.n.m.r. $CDCl_3$): figure 2

7.44-8.08(m) Ph

6.75 (d,d) H_X

5.91 (d,d) H_A

5.46 (d,d) H_B

J_{AX}=17.8 Hz

J_{BX}=10.7 Hz

J_{AB}~0.9 Hz

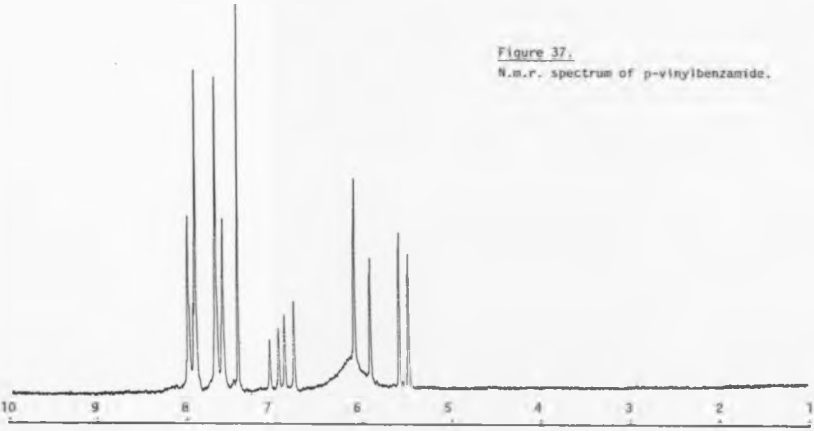


Figure 37.
N.m.r. spectrum of p-vinylbenzamide.

Amide

I.R. (Nujol mull): figure 38

cm^{-1}		
730	C=C	OOP
868	C-H	OOP p-disubstituted aromatic
923	C-H	OOP monosubstituted vinyl
998	C-H	OOP monosubstituted vinyl
1390	C-H	scissor vinyl
1420	C-N	str
1615(s)	C=C	str vinyl
1630	N-H	bend
1667	C=O	str
2900-3000(br)	nujol (C-H str)	
3180	N-H str sym	
3410	N-H str asym	

1.4 Synthesis of p-vinylbenzylamine(10b)

(i) From p-vinylbenzamide only.

Lithium aluminium hydride (4.65 g 0.12 mol) was added to a 1 litre round-bottomed flask containing diethyl ether (dried and distilled off $LiAlH_4$). p-Vinylbenzamide (13.55 g 0.09 mol) was added slowly via a powder funnel. The mixture was refluxed gently for 4.5 days. Excess lithium aluminium hydride was destroyed by careful addition of water. The precipitate produced was filtered off and washed twice with diethyl ether. The filtrate was retained, and the organic layer was separated. The aqueous layer was washed three times with diethyl ether. The ether washings and organic layer were combined and dried over $MgSO_4$. Removal of the solvent yielded 4.3 g (35%) of a viscous yellow oil (10b).

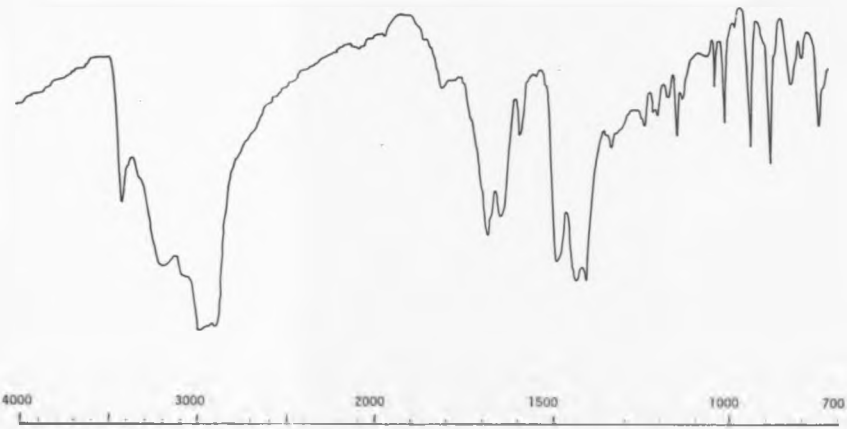


Figure 38. I.R. spectrum of p-vinylbenzamide, (nujol mull).

(ii) From a mixture of p-vinylbenzamide and ammonium chloride

The crude mixture of p-vinylbenzamide (9) and ammonium chloride (7.65 g; containing 5 g amide, 0.034 mol) was placed in the thimble of a Soxhlet apparatus. Lithium aluminium hydride (1.6, 0.042 mol) in diethyl ether (350 ml, dried and distilled off $LiAlH_4$) was placed in the 50 ml round-bottomed flask, and the contents of the thimble were extracted by refluxing over a period of 2 days.

Excess lithium aluminium hydride was destroyed by careful addition of water. After filtration, the aqueous layer was separated, washed three times with ether and the combined organic layers dried over $MgSO_4$. Removal of the solvent yielded 2.67 g (59%) of crude p-vinylbenzylamine (10b) as a viscous yellow oil. A sample for n.m.r. spectroscopy was microdistilled off potassium hydroxide.

The same procedure can be applied to the reduction of the pure amide only. Yield 64%.

^1H n.m.r.($CDCl_3$): figure 4

7.09-7.37(m)Ph
6.68 (d,d) H_X
5.67 (d,d) H_A
5.18 (d,d) H_B
3.80 (s) CH_2
1.47 (s) NH_2
2.61 (q) CH_2 from ethyl impurity
1.20 (t) CH_3 from ethyl impurity

J_{AX}=17.5 Hz
J_{BX}=10.8 Hz
J_{AB}= 1.1 Hz

^{13}C n.m.r ($CDCl_3$): figure 5

141.9	quaternary C on Ph, amine end
135.6	CH vinyl
135.2	quaternary C on Ph, vinyl end
126.4	Ph
125.6	Ph
127.4	Ph of impurity
126.5	Ph of impurity
112.9	CH_2 vinyl
46.0	CH_2 of CH_2NH_2
28.3	CH_2 ethyl impurity
15.5	CH_3 ethyl impurity

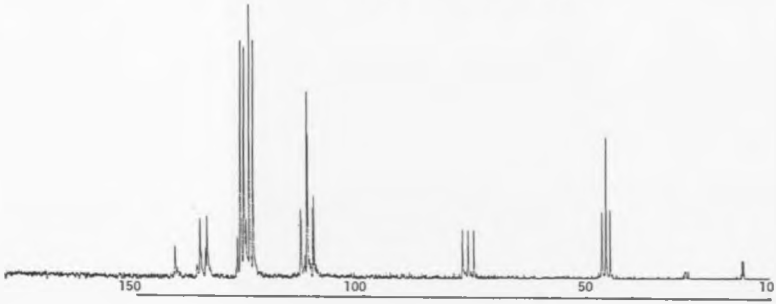
Assignments were confirmed by off-resonance spectrum; figure 39

I.R. (liquid film): figure 40

cm^{-1}	
717	C=C OOP
825	C-H OOP p-disubstituted aromatic
910	C-H OOP monosubstituted vinyl
995	C-H OOP monosubstituted vinyl
1245	C-N str
1332	C-H OOP twist and wag
1410	C-H scissor vinyl
1475	C-H scissor CH_2NH_2
1595	N-H scissor
1615	C=C str vinyl
3000(br)	C-H str vinyl and aromatic
3245	N-H str sym
3300	N-H str asym

Figure 39.

^{13}C n.m.r. spectrum of p-vinylbenzylamine, (off resonance at 52 ppm).



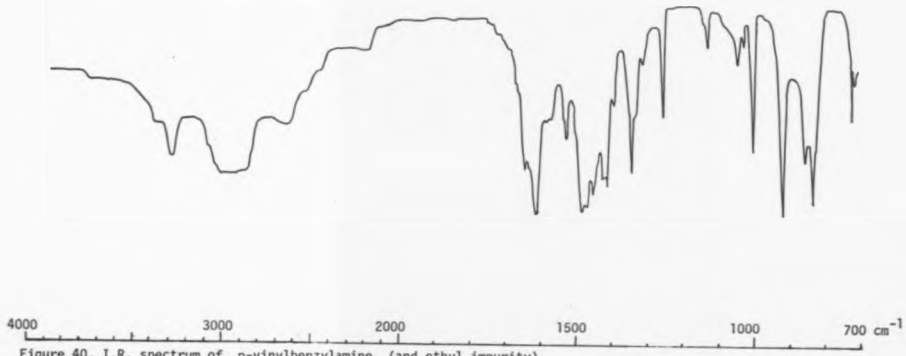


Figure 40. I.R. spectrum of p-vinylbenzylamine (and ethyl impurity).

1.5 Hydrogenation of p-vinylbenzylamine

p-Vinylbenzylamine (10b)(1 g, 0.0075 mol), ethanol (3 ml) and platinum oxide catalyst (0.07 g) were stirred in a 5 ml flat-bottomed flask, at 25 °C under a hydrogen atmosphere. After completion of hydrogen uptake (~ 1.5 hours), the catalyst was filtered, and the solvent removed from the filtrate under reduced pressure. The crude product was microdistilled from NaOH to yield pure p-ethylbenzylamine for spectroscopy.

^{1}H n.m.r.($CDCl_3$): figure 6

7.18(s)	Ph
3.80(s)	CH_2
2.66(q)	CH_2
1.44(s,br)	NH_2
1.25(t)	CH_3

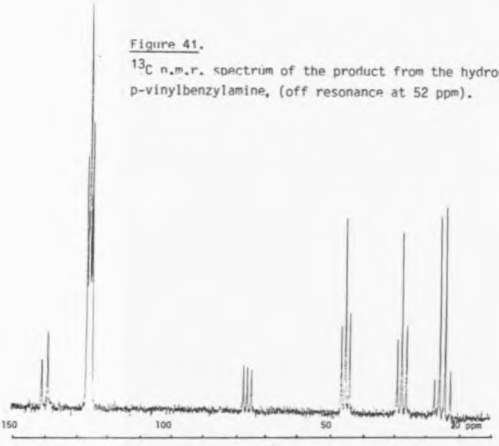
^{13}C n.m.r.($CDCl_3$): figure 7

142.0	quaternary C on Ph (amine end)
140.2	quaternary C on Ph (ethyl end)
127.4	Ph
126.5	Ph
45.9	CH_2 of CH_2NH_2
28.2	CH_2 ethyl
15.5	CH_3 ethyl

Assignments were confirmed by off-resonance spectrum, figure 41.

Figure 41.

^{13}C n.m.r. spectrum of the product from the hydrogenation of p-vinylbenzylamine, (off resonance at 52 ppm).



1.6 Attempted synthesis of methiodide salt of p-vinylbenzylamine

p-Vinylbenzylamine (0.2 g, 0.015 mol) was added to diethyl ether (5 ml, dried over sodium wire), and iodomethane (3 g, 1.3 ml, 0.021 mol) was added. The mixture was left in an ultrasonic bath for 10 minutes. The white precipitate which formed almost immediately became yellow due to the presence of excess iodomethane. The precipitate was filtered, washed with diethyl ether and dried under vacuum at room temperature for 48 hours, but still appeared to be wet.

1.7 Synthesis of p-vinylbenzylformamide (11b)

This synthesis is based on the method of (10b)

The crude p-vinylbenzylamine (10b) (9.32 g,~0.07 mol) was cooled in ice in a 100 ml round bottomed flask and ethyl formate (5.2 g,0.07 mol) was added dropwise with stirring. After refluxing gently for 2 hours, the mixture was stirred at room temperature for 24 hours. Ethanol and any unreacted ethyl formate were removed under vacuum and the residue crystallized from petroleum ether (40-60 ^{o}C)/chloroform to yield 8.6 g pure formamide (11b) (76%)

m.p. 59°C

analysis

	calc:	found:
C	74.53	74.68
H	6.83	6.63
N	8.70	8.75

^{1}H n.m.r. ($CDCl_3$) figure 8

8.10 (s) CHO

7.04-7.28 (m) Ph

6.56 (d,d) H_X

5.90 (s,br) NH

5.59 (d,d) H_A

5.11 (d,d) H_B

4.32 (d) CH_2

J_{NH}=5.8 H_z

J_{AX}=17.7 Hz

J_{BX}=10.9 Hz

J_{AB}=0.9 Hz

Minor resonances at 4.21ppm (CH_2)

7.96ppm (CHO)

due to cis-conformer.

I.R. (nujol mull): figure 42

cm^{-1}	
720	C-H OOP
832	C-H OOP p-disubstituted aromatic
910	C-H OOP monosubstituted vinyl
999	C-H OOP monosubstituted vinyl
1125	C-H vinyl
1250	C-N str $-H_2C-NH-$
1398	C-N str $O=C-N-$
1475	C-H bend
1565	N-H bend
1670(s)	C=O str
2865(sh)	C-H str $\overset{H}{\underset{}{\vert}}C=O$
2900-3000	nujol
3070	C-H str aromatic
3300	N-H str

(B) Synthesis of the monomer m/p-vinylbenzylformamide (11a)

2.1 Synthesis of m/p-vinylbenzylphthalimide (2)

Potassium phthalimide (32 g, 0.17 mol) was dissolved at 40 °C in dimethylformamide (300 ml, dried and distilled off P_2O_5). Chloromethylstyrene (1) (25 g, 0.16 mol) was added and the mixture stirred at 40 °C for 2 hours, and then stirred overnight at room temperature. The resulting white precipitate was filtered and washed with dimethylformamide (100 ml). Chloroform was added to the filtrate, which was then mixed with water (600 ml). The aqueous layer was separated and washed twice with chloroform, and the combined organic layer was washed twice with 2M sodium hydroxide. After drying over $MgSO_4$, the solvent was removed under vacuum. The product was recrystallized from chloroform/petroleum ether (40-60) to yield 36.8 g (85%) m/p-vinylbenzylphthalimide (2).

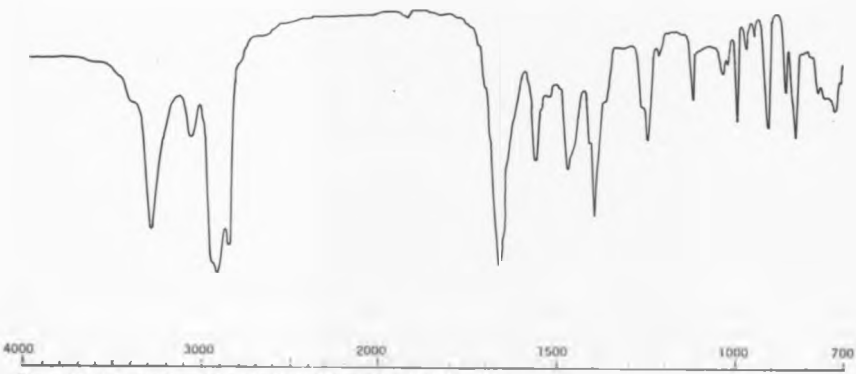


Figure 42. I.R. spectrum of p-vinylbenzylformamide, (nujol mull).

Analysis(%)

	Calc:	found:
C	77.54	77.72
H	4.94	4.97
N	5.32	5.34

^{1}H n.m.r. ($CDCl_3$): figure 43 (m-isomer)

7.60-7.85(m) phthalimide
7.23-7.43(m) Ph
6.67(d,d) H_X
5.71(d,d) H_A
5.21(d,d) H_B
4.80(s) CH_2
J_{AX}=17.7 Hz
J_{BX}=10.8 Hz
J_{AB}=1.0 Hz

Additional resonances due to the minor p-isomer can also be distinguished.

I.R. (KBr disc) figure 19

cm^{-1}	
1720(s)	C = O
1775(w)	C = O

2.2 Synthesis of m/p-vinylbenzylamine (10a)

m/p-Vinylbenzylphthalimide (2) (10 g, 0.041 mol) was dissolved in ethanol (350 ml) at 40 °C. Hydrazine hydrate (3 ml, 0.06 mol) was added and the mixture was stirred overnight at 40 °C. The resulting white solid was filtered, suspended in water (200 ml) and stirred with dilute

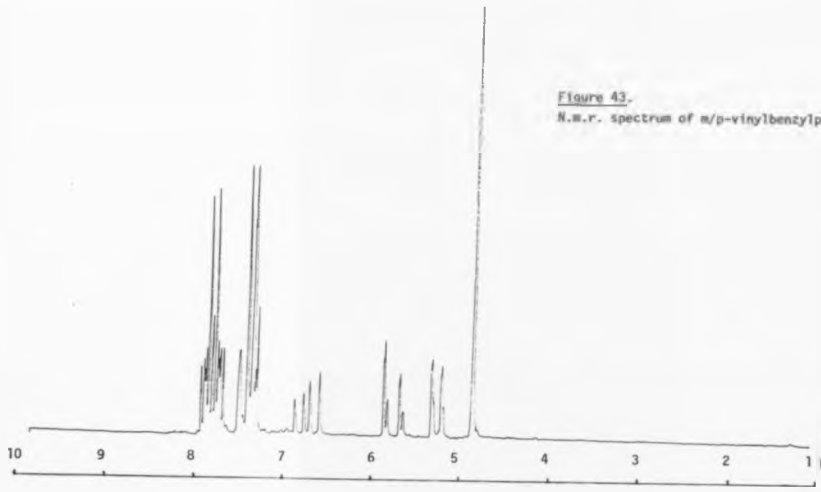


Figure 43.
N.m.r. spectrum of m/p-vinylbenzylphthalimide.

hydrochloric acid (~50 ml) for 1 hour. The remaining solid was filtered off, and the filtrate made basic by the addition of 50% potassium hydroxide. This was extracted (three times) with dichloromethane and dried over $MgSO_4$.*

Ethanol was removed from the original filtrate under vacuum; the residual off-white solid was dissolved in methanol/water (50:50) (300 ml) and filtered. After addition of dichloromethane, the solution was treated with 50% potassium hydroxide (50 ml). The organic layer was separated, and the aqueous layer washed (twice) with dichloromethane. After drying over $MgSO_4$, this was combined with the dichloromethane fraction above (*). Removal of the solvent under vacuum gave 2.1 g (42%) m/p-vinylbenzylamine (10a) as a viscous oil.

I.R. and n.m.r. are identical to those for p-vinylbenzylamine (sect. 1.4) with additional resonances due to the major meta isomer being clearly visible on the ^1H NMR. (Figure 9)

2.3 Synthesis of m/p-vinylbenzylformamide(11a)

This was synthesized from m/p-vinylbenzylamine (10a) by the procedure described in section 2.25.

(C) Polymerization of m/p-vinylbenzylphthalimide

NOTE:

The solubility of m/p-vinylbenzylphthalimide in water at 70 °C was determined to be <0.5g/l.

3.1 Homopolymerization

m/p-Vinylbenzylphthalimide (2) (0.5 g, 0.002 mol) was dissolved in toluene (20 ml) and maintained under a nitrogen atmosphere. Benzoyl peroxide (0.1 g) was added and the mixture heated to 70 °C for 8 hours. Removal of the solvent under reduced pressure yielded ~0.4 g of polymer after drying at 40 °C in a vacuum oven.

I.R.(KBr disc): figure 20

cm^{-1}

1775(w) C = O

1720(s) C = O

3.2 Solution polymerization of m/p-vinylbenzylphthalimide

m/p-Vinylbenzylphthalimide (2) (0.1 g, 0.0004 mol) was dissolved in styrene (3 g, 0.03 mol) and commercial divinylbenzene (1 g, 0.005 mol actual DVB) in 50 ml round-bottomed flask, maintained under nitrogen. Benzoyl peroxide (0.1 g) was dissolved in the mixture and toluene (10 ml) was added. The mixture was stirred at 70 °C for 5 hours and left to cure overnight; (heated and stirred). The material which resulted was fragmented and Soxhlet extracted with dicloromethane. The polymer was dried in a vacuum oven at 40 °C, to yield ~ 3.5 g white powder polymer product which was shown to contain the phthalimide by its infrared spectrum.

I.R.(KBr disc): figure 21

cm^{-1}

1775(w) C = O
1720(s) C = O

3.3 Suspension polymerization of m/p-vinylbenzylphthalimide

The polymerization was carried out under N_2, in at 1 litre baffled reactor, equipped with a high shear stirrer operating a 914 r.p.m. The ask was charged with 500 ml of distilled water and after warming to 70 °C, surfactant [1.2 g of copoly(styrene maleic anhydride)] was added. The monomer mix was prepared from the appropriate amounts of styrene, m/p-vinylbenzylphthalimide (2) and divinylbenzene, (see table 1). After the addition of benzoyl peroxide (0.5 g) and diluent (if used, see table 1), the monomer mixture was added in one portion to the flask and stirred for 5 hours at 70 °C. The product was collected by filtration and washed successively with water, 30% and 50% methylated spirit/water, 100% methylated spirit and finally acetone. After Soxhlet extraction with dichloromethane, the white powder (3) was dried under vacuum.

I.R. (KBr disc): figure 25, for example.

cm^{-1}

1775(w) C = O
1720(s) C = O

Table 1 Polymer data

		% crosslink			
		2	9[c]	52	51
amount phthalimide(2)	g	3.68	7.89	1.84	2.30
	mol %	13.9	14.1	14.0	13.9
amount styrene	g	8.74	15.90	0.26	0.33
	mol %	83.2	71.9	5.0	4.8
amount divinylbenzene[a]	g	0.26	2.46	3.35	4.19
	mol %	1.98	8.83	52.0	51.0
diluent		none	none	toluene (15ml)	heptane/DEB[b] (10ml)
analysis figures for polymer:	C	85.17	86.40	86.30	88.18
	H	6.25	7.00	7.35	7.36[d]
	N	2.18	1.79	1.60	1.78
calculated phthalimide content (mmol g^{-1})		1.56	1.27	1.14	1.27
Exclusion limit (mol wt polystyrene)		-	-	600	700

(a) based on 63% divinylbenzene content of commercial sample

(b) Diluent used heptane + diethylbenzene (9:1)

(c) Several batches of 9% cross-linked resin have been prepared; the figures quoted are for a typical example.

(d) These are average figures from two sets of analyses which gave differing results, particularly for nitrogen content.

(D) Polymerization of p-vinylbenzylformamide and attempted dehydration of the polymer product.

4.1 Homopolymerization

p-Vinylbenzylformamide (11b) (0.25 g, 0.002 mol) was dissolved in toluene (2 ml) and diethylbenzene (2 ml), and maintained under a nitrogen atmosphere. Benzoyl peroxide (0.1 g) was added and the mixture heated to 70 °C for 3 hours. Removal of the solvents under reduced pressure yielded

~0.2 g solid white polymer after drying at 40 °C in a vacuum oven.

I.R. (KBr disc): figure 11

cm^{-1}	
715	N-H rock
820	C-H OOP p-disubstituted aromatic
1241	C-N CH_2-NH_2
1385	C-N O=C-N<
1520	N-H bend
1670(s)	C=O str
2855	C-H str (aldehyde)
2920	C-H str polymer backbone (alphatic)
3058	C-H str aromatic
3300	N-H str

This reaction was repeated on a 10 g scale in an attempt to produce a soluble homopolymer from the p-vinylbenzylformamide. The polymer product was Soxhlet extracted with dichloromethane for 2 days. The dichloromethane was removed under reduced pressure to yield only ~0.25 g of soluble poly (p-vinylbenzylformamide).

4.2 Solution polymerization of p-vinylbenzylformamide 11b

This was carried out in a similar manner to that described for the solution polymerization of m/p-vinylbenzylphthalimide, (sect. 3.2), using the following reagents:

p-vinylbenzylformamide	(2.5 g, 0.0016 mol)
styrene	(21.7 g, 0.21 mol)
commercial divinylbenzene	(0.8 g , 0.004 mol actual DVB)
benzoyl peroxide	(1.25 g)
toluene	(25 ml)

Drying in a vacuum oven at 40 ^{o}C, yielded 21.8 g product as a white powder. The product was seen to contain p-vinylbenzylformamide from the infrared spectrum.

p-vinylbenzyilformamide content of monomer mix

$= 1.55 \times 10^{-2}$ moles in 25 g

$= 0.62$ mmol g^{-1}

Analysis (of solution polymerization product):

found:

C	87.75	
H	7.32	
N	0.96	0.96 N per 10 g solid = 0.68 mmol g^{-1} formamide content of resin product.

I.R. (KBr disc): figure 12

cm^{-1}	
1670	C = O
3350	N - H

A small sample of the above resin was successfully dehydrated using the following procedure:

Resin,(0.5 g, 0.0003 mol) was swollen in dichloromethane (dried over 4Å molecular sieves, 2 ml) and p-toluenesulphonyl chloride (0.3 g, 0.002 mol, freshly recrystallized) was added. Pyridine (10ml, dried and distilled off KOH) was added and the mixture was stirred overnight. After filtration and drying (see sect 5.3(i)), the yield of polymer product was 4.7 g. Titration with HSCN (as described in sect 5.5, see later) gave a figure of 0.34 mmol g^{-1} for isocyanide content.

I.R. (KBr disc): figure 13

cm^{-1}

2140 C ≡ N

4.3 Suspension polymerization

The polymerizations with p-vinylbenzylformamide (11b) were carried out at Polymer Laboratories Ltd, by the author, using the technique described in section 3.3. The following differences were used:

(i) A 2 litre baffled reactor was used, containing 1 litre of distilled water.

(ii) The suspension stabilizer was poly(vinyl alcohol), 88% hydrolysed; 5g.

(iii) The temperature was maintained at 75 °C for 24 hours.

(iiii) In the case of the low crosslinked resins (JCPL20,21,22) the suspensions were centrifuged to separate the polymer, as some difficulty was experienced in filtration.

I.R. (KBr disc): figure 18

cm^{-1}

1720 C = O

Exclusion limits:

See figures 44-47 and table 2.

Table 2 Suspension polymerization of p-vinylbenzylformamide

Number	g styrene	mol% styrene	g formamide (a)	mol% formamide (a)	g commercial DVB(b),(c)	mol% actual DVB(b),(c)	diluent	amount diluent (ml)	Exclusion limit (f)	micro-analysis (%)(d)	analysis calc'd as mmolg $^{-1}$
JCPL5	-	-	1.0	12.35	9.0	87.65	heptane	11	80,000	0.51	0.36
JCPL8	-	-	1.5	24.28	6.0	75.72	heptane	7.5	3,400	0.83	0.59
JCPL9	-	-	1.5	24.28	6.0	75.72	heptane	10.5	solid-no pores	0.87	0.62
JCPL11	-	-	1.0	12.35	9.0	87.65	diethyl benzene	10.5	16,000	0.64(e)	0.45(e)
JCPL20	8.71	91.70	1.0	6.77	0.3	1.53	-	-	-	0.39	0.28
JCPL21	8.22	88.76	1.0	6.97	0.8	4.27	-	-	-	0.39	0.28
JCPL22	7.41	83.62	1.0	7.30	1.6	9.07	-	-	-	0.24	0.17

(a) p-vinylbenzylformamide (11b)

(b) divinylbenzene

(c) calculated for commercial DVB = 63% actual DVB

(d) calculated fom %N microanalysis figures

(e) calculated as an average of two separate sets determined

(f) determined at Polymer Laboratories (by Z. Dryzek)

Figure 44.
Determination of the exclusion limit for polymer JCPL5.

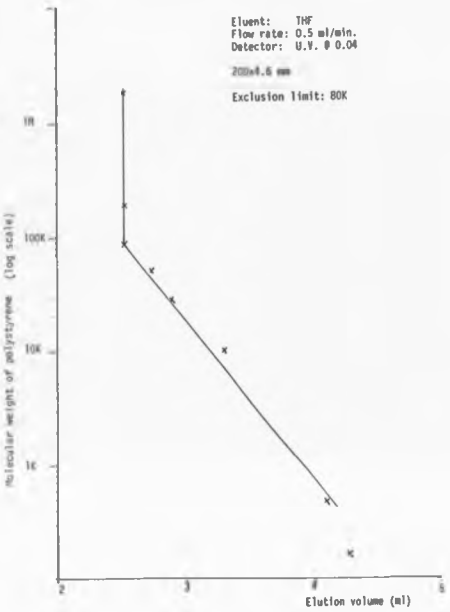


Figure 45.
Determination of the exclusion limit for polymer JCPL8.

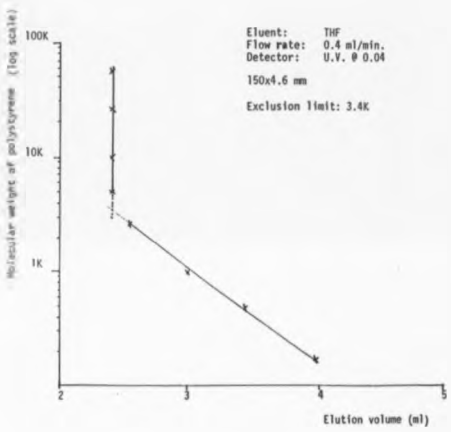


Figure 46.
Determination of the exclusion limit for polymer JCPL9.

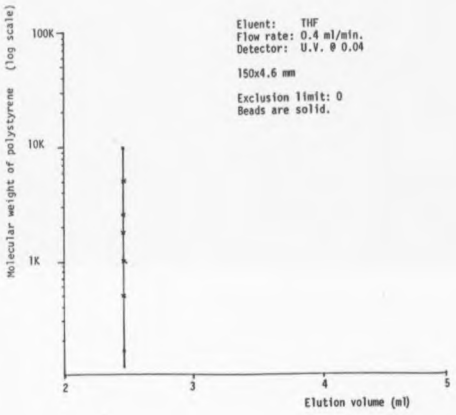
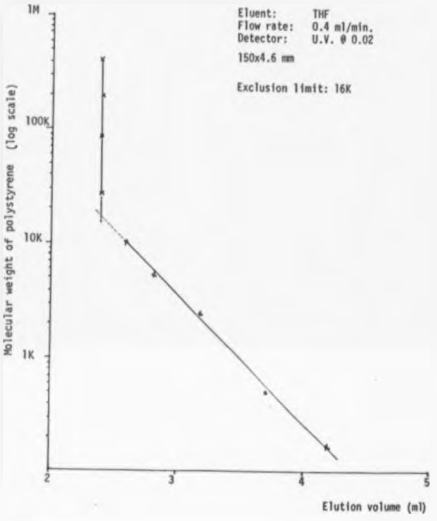


Figure 47.
Determination of the exclusion limit for polymer JCPL11.



4.4 Dehydration of polymer-supported formamide

(a) Using p-toluenesulphonyl chloride and pyridine

Small samples (0.5 g) of resins were treated as described in section 5.3(i) (see later). Little or no isocyanide resulted.

Typically:

For JCPL11, product when titrated with HSCN gave a figure of 0.12 mmol g^{-1} isocyanide and a small I.R. peak, ν_{NC} at 2140 cm^{-1} (KBr).

(b) Using diphosgene and triethylamine, method (i) - based on the method of Efraty et al[7]

Resin JCPL11 (0.5 g, maximum 10% formamide = 0.00031 mol) swollen in dichloromethane, (21 ml, dried over 4Å molecular sieves) and triethylamine (6 ml, 0.10 mol, dried and distilled off KOH) were refluxed for 30 minutes. Diphosgene (1 ml, 0.008 mol) in dichloromethane (6 ml, dried as above) was added dropwise. The mixture was refluxed for a further 30 minutes after the addition was complete. The polymer was filtered, washed successively with water, absolute ethanol and ether, and dried under vacuum.

Again, only a very small amount of isocyanide resulted; 0.09 mmol g^{-1} by HSCN titration.

Method (ii)

Essentially the same as in (i) except that the reaction mixture was refluxed for 3 days.

Titration with HSCN gave an isocyanide content of 0.065 mmol g^{-1}.

I.R. (KBr disc):

ν_{NC} 2140cm^{-1} (v.weak)

Method (iii) based on the method of Ugi and Skorna.[27]

Resin (0.5 g, maximum 10% formamide,= 0.00031 mol) swollen in dichloromethane,(10 ml, dried over 4Å molecular sieves) and triethylamine (1 ml,0.017 mol) were placed in a 100 ml round-bottomed flask, fitted with a drikold condenser. The flask was cooled in ice during the dropwise addition of diphosgene (1 ml, 0.008 mol) in dichloromethane (10 ml, dried as above). The contents of the flask were stirred and maintained at 0 °C for a further 2 hours, and then stirred at room temperature for 24 hours. The polymer was filtered, washed successively with water, absolute ethanol and finally ether, and dried under vacuum.

No isocyanide was present according to the HSCN titration, and no ν_{NC} stretch was seen on the infrared spectrum.

4.5 Synthesis and attempted hydrolysis of benzylformamide

(i) Synthesis

Benzyl formamide was synthesized from benzylamine according to the method described in section 1.7 (84%).

N.m.r. ($CDCl_3$) (figure 17)

7.95(s) CHO

7.14(s) Ph

4.27(d) CH_2

Additional resonances at 7.78 and 4.14 due to cis-conformer (see discussion; detailed for p-vinylbenzylformamide)

I.R. (nujol mull) (figure 16)

1300-3500 only shown

cm^{-1}

1380(s) C-N (H-C-N-CH_2)

1465(s) C-H bend

1550(w) C-N (-N-CH_2-)

1650(s) C=O str

2800-3100(s) C-H aromatic + aliphatic + nujol

3290(m) N-H str

(ii) Attempted hydrolysis of benzyl formamide

Benzyl formamide (5 g, 0.004 mol) was dissolved in dichloromethane (20 ml) and stirred in distilled water (300 ml) for 5 hours at 70 ^{o}C. The mixture was then stirred at room temperature for a further 48 hours . The organic layer was separated, and the aqueous layer was extracted three times with dichloromethane . The combined organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure, to yield a white solid product.(4.9 g).

N.m.r. ($CDCl_3$)

As for product in section 4.5(i)

I.R. (nujol mull)

As for product in section 4.5(i)

(E) Synthesis of the polymer-supported isocyanide (6)

Syntheses described in this section are examples of those performed for the 9% crosslinked resin. Similar reactions were carried out for the 2% and 52% crosslinked resins also.

5.1 Synthesis of the polymer-supported amine (4)

Method (i) using hydrazine hydrate

Polymer-supported phthalimide (3) (27 g, 0.029 mol phthalimide) was suspended in ethanol (400 ml) and hydrazine hydrate (30 ml, 0.62 mol) was added. The mixture was refluxed and stirred for 24 hours, then filtered and washed with water to dissolve the white precipitate which had formed. The white polymer (4) was then washed successively with ethanol, ether and dichloromethane, and dried under vacuum.

The amine content was determined according to the method described in section 5.4. The following variations on the above technique were tested, but no significant improvement in amine yield was seen:

(1) Extended reaction time - up to 5 days (in one day intervals).
(2) Addition of dichloromethane to swell the resin.
(3) Reaction flask placed in an ultrasonic bath for 24 hours.
(4) Addition of tetrahydrofuran to swell the resin.

Method (ii) using methylamine

Polymer-supported phthalimide (3) (2 g, 0.002 mol) was swollen in dichloromethane (10 ml) and 40% methylamine solution (8 ml, 0.1 mol) was added. The mixture was shaken for 24 hours, and the polymer filtered, washed successively with water, methanol, and dichloromethane and dried under vacuum.

The amine content was determined according to the method described in section 5.4.

In a direct comparison of methods(i) and (ii) i.e. using the same batch of polymer-supported phthalimide, the following results were obtained:

method (i) using hydrazine hydrate :amine content=1.24 mmol g^{-1}

method (ii) using methylamine (aq soln):amine content=1.08 mmol g^{-1}

Table 3 Phthalimide content and corresponding amine content of resins

batch no.	phthalimide content from micro-analysis mmol g^{-1} (a)	amine content expected (micro-analysis) mmol g^{-1} (b),(k)	amine content from picrate det.n mmol g^{-1} (c)	type of resin	% crosslink
JC83	1.15	1.36	1.24[e]	gel-type	9
			1.08[f]	gel-type	9
JC90	1.27	1.53	1.27	gel-type	9
			1.21	gel-type	9
JC107	1.96 1.28[d]	1.54	0.63[g]	macroporous	51[h]
	0.59		0.49[g]	macroporous	51[h]
JC109	1.39	1.71	1.53	gel-type	9
JC134	1.10	1.29	1.04	gel-type	9
JC205	1.08	1.26	1.43	gel-type	9
JC213	1.32	1.60	1.86	gel-type	2
	1.56	1.97		gel-type	
JC216	1.14	1.34	0.77	macroporous	51[i]

(a) Error in analysis + 0.2 mmol g^{-1} (calculated after each individual figure).

(b) Error in calculation + 0.2 mmol g^{-1} as these are calculated from figures from phthalimide microanalysis.

(c) Error in picrate determination + 0.2 mmol g^{-1} determined by blank determination on resin with no amine present.

(d) Samples from the same batch; average value used in further calculations.

(e) Synthesis using hydrazine hydrate.

(f) Synthesis using aq. methylamine.

(g) These two determinations were performed on different samples from the same batch of resin, but do not correspond exactly to the figures on the same line.

(h) Heptane/diethylbenzene diluent system used in polymerization.

(i) Toluene diluent used in polymerization.

(k) Calculated from the phthalimide content of the polymer and alowing for the weight loss experienced in the conversion of phthalimide(3) to (4).

5.2 Synthesis of the polymer-support formamide (11a)
(Based on the method of Vail, Moran, and Moore.)[28]

Polymer-supported amine (4) (20g, 0.029mol amine) was suspended in ethyl formate (170 ml) and refluxed for 24 hours. The white polymer product (5) was filtered, washed with diethyl ether and then pentane and dried under vacuum.

I.R. (KBr disc): figure 27
ν_{CO} 1670(s) cm^{-1}.

5.3 Synthesis of the polymer supported isocyanide(6)

Method (i) using p-toluenesulphonyl chloride and pyridine
(Based on the method of Hertler and Corey).[29]

Polymer-supported formamide (5) (7 g, ~0.01 mol formamide) was swollen in dichloromethane (70 ml, dried over 4A molecular sieves), followed by the addition of p-toluenesulphonyl chloride (12.5 g, 0.006 mol, freshly recrystallized). Pyridine (280 ml, dried and distilled off KOH) and aniline (2 ml) were added and the suspension stirred under nitrogen for 16

hours. The light yellow-brown polymer (6) was filtered, washed successively with water, ethanol and dichloromethane, and dried under vacuum.

The isocyanide content was determined by the method described in section 5.5.

An improvement in isocyanide yield was observed when the volume of pyridine used was increased from approximately 10x weight of resin to 40x, in ml. The figure quoted, 280 ml is the latter. Early batches of isocyanide were synthesized with less pyridine present.

I.R. (KBr disc): figure 29

$\bar{\nu}_{NC}$ 2140(s)cm^{-1}

Method (ii) using phosgene and triethylamine

Attempt (1)

Polymer-supported formamide (5) (3 g, ~0.004 mol) was swollen in dichloromethane (60 ml, dried over 4Å molecular sieves) in a 250 ml round-bottomed flask, with an extended side-arm. Triethylamine (2 ml, 0.0014 mol, dried and distilled off KOH) was added to the flask and the mixture stirred at room temperature. Phosgene (1.1 ml, 0.015 mol) was condensed into graduated apparatus, and then allowed to warm up and to bubble through into the reaction flask. The mixture was then stirred for a further 2 hours and then nitrogen was piped through the apparatus to force any unused phosgene into the sodium hydroxide trap to destroy it.

The polymer was filtered, washed successively with water, methanol and dichloromethane, then dried under reduced pressure. The isocyanide content was determined as described in section 5.5.

Isocyanide content : 0.7 mmol g^{-1}

I.R. (KBr disc): figure 28a

ν_{NC} 2140(s) cm^{-1}

ν_{CO} 1670(s) cm^{-1}

Although an excess of phosgene was used a considerable amount of unreacted formamide was present (from I.R. spectrum).

Phosgene is a highly toxic gas. Extreme care must be used when handling this material. It can be destroyed by reaction with NaOH, and its presence can be detected using a test filter paper. This filter paper is prepared by soaking in a 10% solution of diphenylamine and p-dimethylaminobenzaldehyde (1:1) in ethanol; and is then dried. In the presence of phosgene, the filter paper becomes bright yellow or orange.

Attempt (2)

The reaction was repeated as described in attempt (1), but the amount of phosgene was increased by 4 fold.

I.R. (KBr disc): figure 28b

No ν_{NC} stretch

ν_{CO} very broad 1700-1800cm^{-1}

Method (iii) using diphosgene and triethylamine

The method used was similar to that described in section 4.4(b), method (iii). Two attempts were made using (a) approximately 1 equivalent diphosgene and (b) a 10 fold excess of diphosgene.

The actual amounts of reagents used were as follows:
polymer-supported formamide (5),(0.5 g, 0.0006 mol) dichloromethane (8 ml, dried over 4Å molecular sieves) triethylamine (0.5 ml, 0.004 mol, dried and distilled off KOH)
Diphosgene (a) 0.1 ml, 0.0008 mol
(b) 1.0 ml, 0.0008 mol each in 5 ml dry CH_2Cl_2

I.R. (KBr disc): figure 48
(a) Extremely small ν_{NC} at 2140cm^{-1}
ν_{CO} 1670(s)cm^{-1}
(b) No ν_{NC} stretch
ν_{CO} very broad band 1700-1800cm^{-1}

5.4 The determination of the amine content of the resin (4)

This was carried out according to the method of B.F.Gisin[17], except that the times quoted in the article were not adhered to. The actual procedure used was as described below:

The polymer-supported amine (4) (0.1 g, accurately weighed) was placed in a specially designed, very small column, containing a sinter. The resin was swollen in dichloromethane for 5 minutes, and then the solvent was run off. The resin was washed twice with 5%(v/v) diisopropylethylamine in dichloromethane, each time letting the solution run off the column slowly. The resin was washed five times with dichloromethane, and then treated with 0.1 M picric acid in dichloromethane. Excess picric acid solution was washed off with dichloromethane - washing was continued until no yellow colour was visible in the solution washed off the column. The picrate was then eluted by treating the resin with the above diisopropylethylamine solution and the washings were collected in a 50 ml volumetric flask. After 5 washings, the diisopropylethylamine solution was left on the column

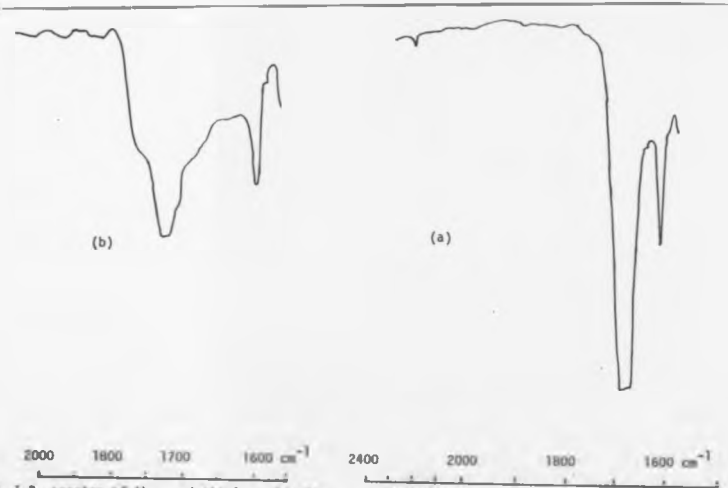


Figure 48. I.R. spectra of the products from the attempted dehydration of the palymer-supported isocyanide using (b) excess diphosgene or (a) 1 equiv. diphosgene.

for 24 hours; then washing was continued as before. When no further yellow colour was seen in the diisopropylethylamine washings, the resin was washed with dichloromethane until 50 ml had been collected. The yellow solution collected was then diluted (2 ml into 100 ml) with 95% ethanol and its absorbance measured spectrophotometrically at 358 nm. The amine content of the resin can then be calculated as illustrated in the example below: (Amine content = picrate concentration of solution washed off column).

For JC111. (see figure 49).

Absorbance at 358nm=0.899

$$\text{conc}=\frac{\text{abs}}{\text{E}\,l}$$

E=molar absorbtivity=14,500 mol^{-1} dm^2

l=cell path length=1 cm

$$\text{therefore } \frac{0.899}{14500 \times 1} \times \frac{100^*}{40} = 1.55 \times 10^{-4} \text{ mol per } 0.1010\text{g}$$

therefore amine content=1.53×10^{-3} mol g^{-1}

*for dilution

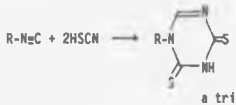
(for table of results see p158).

5.5 The determination of the isocyanide content of the resin (6)

The isocyanide content was determined using a modified version of the method of Arora, von Hinrichs and Ugi.[20] The reagents were prepared according to this reference. The 0.1 M HCl solution was standardized against a standard 0.1 M borax solution. The 0.1 M triethylamine solution was standardized against the 0.1 M HCl solution. The 0.1 M thiocyanic acid was then standardizsed against the 0.1 M triethylamine. The isocyanide reacts with the thiocyanic acid according to the equation shown, and the excess acid is back titrated against the standard triethylamine solution.

Figure 49.
Determination of the amine content of resin JC111.

Date: 24/9/86
Sample identity: JC-111
Ordinate Maximum 1.209
Ordinate Minimum 0.000
Upper Wavelength 700.0 nm.
Lower Wavelength 190.0 nm.
Scan Speed 400.0 nm/min.
Bandwidth 1.0 nm.
Time Constant 0.2 sec



a triazinedithione.

Procedure:

0.1 g of polymer-supported isocyanide (6) was swollen in 5 ml of 1:1 ethyl acetate/dichloromethane, followed by addition of 3 ml of 0.1 M HSCN in ethyl acetate. After standing for 30 minutes, indicator (0.2% solution of methylene blue and neutral red (1:1) in methanol) and dimethylformamide (2 ml)were added and the excess HSCN was back-titrated against the standard 0.1 M NEt_3.

Table 4

Isocyanide and amine content of various batches of resin.

Amine content of resin (4)[a] mmol g^{-1}	Isocyanide content of resin (6)[b] mmol g^{-1}
1.27	0.48
1.27	0.71[c]
1.21	0.57
1.21	0.56
1.21	0.57
1.21	0.61
1.27	0.84[d]
1.43	0.90[d]
1.43	1.03[d]

(a) by picrate determination

(b) by HSCN titration

(c) dehydrated using phosgene in triethylamine; all others by p-toluenesulphonyl chloride in pyridine.

(d) volume of pyridine used in dehydration increased.

(f) Synthesis and polymerization of allylformamide

6.1 Synthesis of allylformamide

Allylformamide was prepared from allylamine using the method described in section 1.7. the following reagents were used:

allylamine (119.7 ml, 91 g, 1.59 mol)

ethyl formate (128.2 ml, 118 g, 1.59 mol)

The crude liquid product was distilled under reduced pressure (55 °C at 0.3 mm Hg) to yield 109.4 g (81%) pure allylformamide.

^{1}H n.m.r. ($CDCl_3$): figure 50

8.17(s) CHO

7.23(s,br) NH

4.93-6.15(m) CH_2=CH- allyl

3.92(t) CH_2

D_2O exchange: figure 51

7.23(s,br) disappears

3.92(t) becomes (d)

6.2 Polymerization of allylformamide

Several test-tube polymerizations were carried out, attempting to copolymerize allylformamide with styrene and/or divinylbenzene,or methacrylic acid or acrylic acid. (See table 5)

Typically:

The monomers were placed in a test-tube or boiling tube and the initiator (0.1 g, benzoyl peroxide or azoisobutyronitrile) was added to the mixture, maintained under nitrogen. Any solvent used was then added. The test-tube or boiling tube was then immersed in an oil bath at 80 °C for

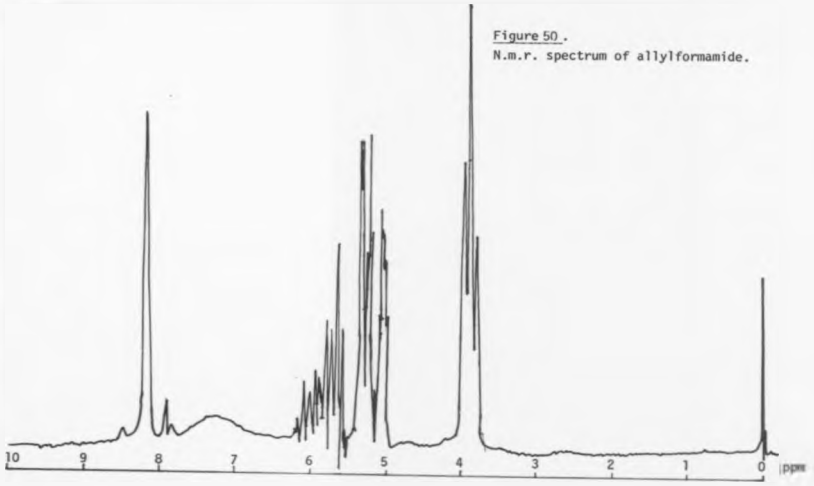
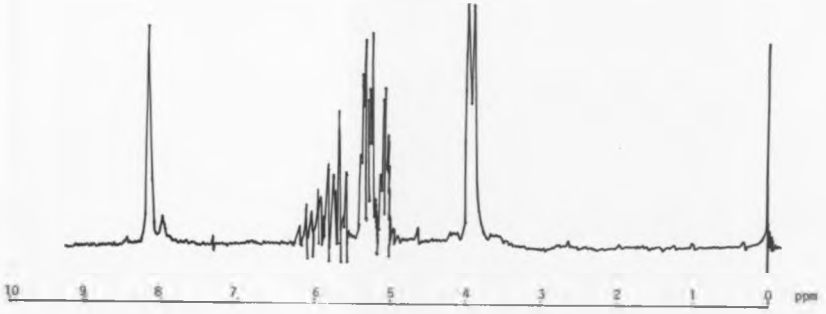


Figure 50.
N.m.r. spectrum of allylformamide.

Figure 51.
N.m.r. spectrum of allylformamide, D_2O exchange.



5 hours. If a solvent was used and the polymer remained in solution, diethyl ether was added to precipitate the polymer. The polymer product was filtered, washed with ethanol and ether and dried under vacuum. If the polymer had formed as a solid "lump" it was then ground up with a mortar and pestle before further use.

6.3 Attempted synthesis of the supported isocyanide

After Soxhlet extraction with dichloromethane dehydration of the formamide to the isocyanide was attempted.

(i) Using diphosgene and triethylamine

The procedures as described in section 4.4(b) were tried on sample JC31a.

(ii) Using p-toluenesulphonyl chloride and pyridine

The procedure as described in section 5.3(i) was tried on samples JC31a and JCPL12.

In all attempts no isocyanide was produced

i.e. no ν_{NC} present on spectrum

ν_{CO} 1700 cm^{-1} still present for JC31a

Table 5 Polymerization experiments using allylformamide

g allyl formamide	g styrene	g commercial DVB	g acrylic acid	g methacrylic	Analysis %N(d)	initiator	solvent (ml) if used	sample number
1	-	-	-	-	-	B.P(b)	toluene 1ml	JC15(a)
1	-	-	-	-	-	azbn(c)	toluene 1ml	JC16(a)
1.5	3.5	-	-	-	2.08	azbn	-	JCPL12
2.5	-	7.5	-	-	0.00	B.P	-	JCPL17
1	1	1	-	-	0.97	B.P	-	JC44
1	-	1	-	-	1.11	B.P	-	JC45
1.5	3.5	1	-	-	2.51	B.P	-	JC49
2	4	0.6	-	-	1.58	B.P	-	JC5D
2	3	0.1	-	-	0.76	B.P	-	JC51
1.5	3.5	0.7	-	-	1.04	B.P	-	JC53
1.25	2.25	1.5	-	-	0.27(g)	B.P	-	JC54
2.5	-	-	7.5	-	2.81	azbn	-	JCPL14
5	-	-	2.5	-	5.10	azbn	EtOH 8ml(f)	JC62
5	-	-	-	2.5	4.67	azbn	EtOH 8ml(f)	JC31(e)
1.35	-	-	-	0.68	4.22	azbn	EtoH 8ml(f)	JC29

(a) no polymerization
(b) benzoyl peroxide = B.P
(c) azoisobutyronitrile = azbn
(d) analysed before Soxhlet extraction
(e) became JC31a after Soxhlet extraction %N=3.75
(f) polymer precipitated by pouring into 20ml diethyl ether
(g)error of analysis is $\pm$ 0.3

ν_{CO} for allylformamide 1700 cm^{-1}, hidden in copolymers with methacrylic or acrylic acid by ν_{CO} of acid very broad ~ 1720 cm^{-1}.

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CHAPTER THREE : METAL COMPLEXATION USING POLYMER-SUPPORTED ISOCYANIDES

3.1 INTRODUCTION

Although the complexing properties of monomeric isocyanides have been extensively investigated in the last 20-30 years, only very recently have the complexing properties of polymeric analogues been investigated. During the course of our work, Arshady et al have reported complexation[1,2] using an acrylamide based polymer prepared by suspension copolymerization[3] (in 1,2-dichloroethane) of dimethylacrylamide, 3-formamidopropyl acetate and bis-acrylamide (the crosslinking agent) based on earlier work by Arshady and Ugi[4a,4b]. These polymer supports are compatible with a wide range of solvents, such as water, methanol, dichloromethane and benzene.

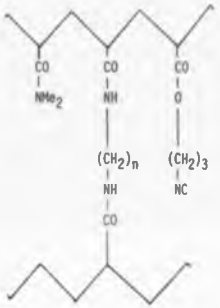


Fig 1. Acrylamide based polymer support.

This acrylamide based resin was also the basis for a new polymerization technique in which the copolymerization of differentially soluble monomers is carried out after being absorbed onto beads of such a resin (referred to as the prepolymer support.)[4]

The resin shown in figure 1 reacts with various transition metal salts; $RhCl_3.3H_2O$, $Cu(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Cu(acac)_2$ as well as organometallic complexes such as $Mo(CO)_6$ and $Rh(PPh_3)_3Cl$. Complexation was observed in all cases, with the exception of the nickel salt which caused polymerization of the isocyanide group[1]. A polymer-supported isocyanide-palladium chloride was found to exhibit catalytic properties in some hydrogenations[2].

An investigation of the reaction of various metal carbonyl complexes with polymer-supported isocyanides has also been carried out using a styrene/divinylbenzene based support. The catalytic activity of the supported rhodium carbonyl complex for hydrogenation was also investigated[5].

Silica has also been used as a support for the isocyanide group, by condensation of $(EtO)_3Si(CH_2)_3NC$ with high surface area silica. The resulting functionalized silica was reacted with the rhodium dimers $[Rh(cod)Cl]_2$ and $[Rh(CO)_2Cl]_2$ to yield active hydrogenation catalysts (for the hydrogenation of cyclohexene to cyclohexane), although reduction to metallic rhodium was thought to be responsible for the catalytic activity[6,7].

This chapter describes the complexation experiments carried out using the polymer-supported isocyanide whose synthesis has been described in chapter 2.

3.2 RESULTS AND DISCUSSION

The isocyanide group has been generated on a polystyrene support by the methods described in chapter 2, and resins having 2% and 9% crosslink ratios have been produced. These polymer resins may be swollen in organic solvents such as dichloromethane, toluene and tetrahydrofuran, thus enabling the complexation of low valent neutral organometallic complexes from toluene or tetrahydrofuran, and of anhydrous metal chlorides from tetrahydrofuran. The polymers retain sufficient swellability in 50% aqueous tetrahydrofuran such that the complexation of metal salts which are soluble in this medium may also be studied.

Although 2% crosslinked resins were used in some complexation studies, the 9% crosslinked resins were predominately used and the results described in this chapter have been obtained with the latter unless otherwise stated.

(1) Infrared spectra

As infrared spectroscopy and analytical data are the only readily available means of establishing the nature of the supported complex, a brief discussion of the infrared spectra of isocyanide-metal complexes is given here.

The isocyanide C≡N stretching band is usually observed in the range 2120 - 2180 cm^{-1} for free monomeric isocyanides, and the polymer-supported isocyanide prepared also falls into this range, having a sharp isocyanide band at 2140 cm^{-1}. Some examples of monomeric isocyanides are given below:

	ν_{NC} cm^{-1}	Reference
methyl isocyanide	2170	8
t-butyl isocyanide	2131	9
p-toluenesulphonylmethyl isocyanide	2155	10
1,1,3,3-tetramethylbutyl isocyanide	2126	9

A change in the infrared isocyanide stretching frequency is observed upon complexation, and the position and multiplicity of the complexed band give some indication of the structure of the product. In the case of the supported isocyanide, the band also becomes broader on complexation. Generally, a decrease in the isocyanide stretching frequency is found when the ligand is complexed to metals in either low or zerovalent oxidation states. Cotton and Zingales[11] record the values of 2070, 2012 and 1965 cm^{-1} respectively for the isocyanide stretching frequency for the zerovalent chromium complex, $(C_6H_5NC)_6Cr$, which is considerably lower than that of the free ligand, (C_6H_5NC) at 2136 cm^{-1}. (Note that a later article[12] claims the band at 2070 cm^{-1} for the complex is present only in impure samples.) A value of around 1700 cm^{-1} is usually observed for bridging isocyanides, for example for the platinum complex $Pt_3(CNBu^t)_6$ the isocyanide stretching frequencies are recorded at 2155 cm^{-1} (terminal) and 1714 cm^{-1} (bridging)[13]. The lowering of the isocyanide stretching frequency is usually taken to indicate a significant amount of back donation of electrons from the metal into vacant π^* orbitals on the isocyanide. In such examples, the isocyanide is acting both as a sigma donor and a pi acceptor molecule, in a manner similar to that often exhibited by carbon monoxide. However, when the isocyanide is complexed to a metal in an intermediate or high oxidation state, the position of the infrared band is moved to higher frequency by as much as 150 cm^{-1}. This increase in stretching frequency can be further quantified, as it is found that the increasing the oxidation state of the metal directly increases the isocyanide infrared stretching frequency. This can be seen from the examples given overleaf:

	Oxidation state of metal	$\bar{\nu}_{NC}$ cm^{-1}	Reference
Palladium:			
cis-$[PdCl_2(CNMe)_2]$	II	2280 2264	14
$[PdCl(CNMe)_3][PF_6]$	II	2300 2292 2282	14
$[PdCl(CNBu^t)_2]_2$	I	2166	15
Platinum:			
$[NBu^n_4][PtCl_3(CNMe)]$	II	2240	14
cis-$[PtCl_2(CNMe)_2]$	II	2281 2153	14
$[NBu^n_4][PtCl_5(CNMe)]$	IV	2309	11
cis-$[PtCl_4(CNMe)_2]$	IV	2322 2314	14
Copper:			
$[Cu(CNBu^t)_4(H_2O)_2][ClO_4]_2$	II	2233	9
$[Cu(CNBu^t)_4][ClO_4]$	I	2181	9

The isocyanide is assumed to be acting principally as a sigma donor in these examples, and on going from metal(I) to metal(II) the change in oxidation state causes an increase in the electrostatic effect, with a corresponding decrease in the amount of back donation of electrons from the metal to the ligand. This effectively increases the strength of the C-N bond, resulting in a move to higher frequency for the isocyanide infrared stretching band, the increase being greatest for the higher oxidation states.

The position of the isocyanide band is also dependant on the number of isocyanide ligands which are co-ordinated. For a metal in a fixed oxidation state, surrounded by a variable number of isocyanide ligands, the isocyanide stretching frequency increases as the number of isocyanide ligands increases. This is illustrated by the example given below for platinum. However several examples exist where this is not observed such as shown for silver, below:

	Oxidation state of metal	ν_{NC} cm^{-1}	Reference
Platinum:			
$[PtCl(CNMe)_3][PF_6]$	II	2308	14
		2288	
		2287	
$[Pt(CNMe)_4][PF_6]_2$	II	2322	14
		2314	
		2284	
Silver:			
$AgNO_3$(p-tolylNC)$_2$	I	2195	11
$AgClO_4$(p-tolylNC)$_4$	I	2186(sh)	11
		2177 (s)	
		2136 (w)	

A difference is also observed between alkyl and aryl isocyanides in similar metal complexes. In general an increase of around 50 cm^{-1} is found for the alkyl isocyanide complex in comparison with the aryl analogue.

For example:

	ν_{NC} cm^{-1}	Reference
$(p\text{-tolylNC})_6MnI$	2090	11
	2035(w)	
$(CH_3NC)_6MnI$	2129	11

(2) Complexation of metal salts from aqueous tetrahydrofuran.

Generally, the polymer-supported isocyanide was swollen in tetrahydrofuran and an appropriate excess of the metal salt (usually M:NC approximately 2:1) dissolved in an equal volume of water was added. (The exact quantities used vary slightly due to the solubility of the salts in this medium). The solubility of these complexes in the aqueous tetrahydrofuran medium used was confirmed by dissolving the metal salt in the appropriate amount of distilled water (usually 5 ml), followed by the addition of an equal volume of tetrahydrofuran; no precipitation (or reaction) was observed. Virtually quantitative complexation is observed in all cases where metal complexation is found, as confirmed by the complete (or almost complete) disappearance of the sharp isocyanide vibration of the free isocyanide. This is replaced by a broadened band at higher frequency for all positive oxidation state metal complexes, except for one example of Rh(I). The spectra of the isocyanide-metal complexes are reproduced throughout this section, but table 1 summarizes the results. Analytical data (in mmol g^{-1}) for metal, chlorine and phosphorus together with values calculated on the basis of proposed complexation reactions, are given in table 2. Together with a comparison of the infrared spectra to those of "model compounds" (see table 1), the infrared

Table 1 Infrared Data.

supported complex	observed ν_{NC} cm^{-1}	"model" complex	observed ν_{NC} cm^{-1}	reference
K_2PtCl_4	2222	cis-$PtCl_2(CNMe)_2$	2281	14
			2253	
		$[Bu^n{}_4N][PtCl_3(CNMe)]$	2240	14
		$[PtCl(CNMe)_3][PF_6]$	2308	14
			2288	14
			2287	
		$[Pt(CNMe)_4][PF_6]_2$	2322	14
			2314	
			2284	
Na_2PdCl_4	2260	cis-$PdCl_2(CNMe)_2$	2280	14
		$[PdCl_2(CNC_7H_7)]_2$	2220	25
		$[PdCl(CNBu^t)_2]_2$	2166	15
$RhCl_3.xH_2O$	2214	$[Rh(CNMe)_4][BPh_4]$	2197	29
		$[Rh(CNMe)_4Cl_2][PF_6]$	2280	55
		$[Rh(CNMe)_4I_2][BPh_4]$	2265	29
		$Rh(CNMe)_3I_3$	2242	29

supported complex	observed ν_{NC} cm^{-1}	"model" complex	observed ν_{NC} cm^{-1}	reference
$AgNO_3$	2220	$[Ag(CNCy)_2][ClO_4]$	2215	33
			2190	
$AgPF_6$	2238	$[Ag(CNCy)_4][ClO_4]$	2188	33
			2150	
		$[Ag(CNBu^t)_3][PF_6]$	2241	32
			2184	
		$[Ag(CNCH_2SO_2C_6H_4CH_3)_2][BF_4]$	2230	10
$HgCl_2$	2265	$HgCl_2(CNBu^t)$	2245	40
$CoCl_2$	2225	$CoCl_2(CNMe)_4$	2227	8
		$CoCl_2(CNMe)_2$	2260	8
		$[Co(CNMe)_5][ClO_4]$	2198	23
			2139	
$FeCl_2$	2190	$cis\text{-}FeCl_2(CNp\text{-}MeOC_6H_4)_4$	2195	48
			2160	
			2140	
		$[Fe(p\text{-}CH_3C_6H_4NC)_6][ClO_4]_2$	2190	49
		$[FeCl(p\text{-}CH_3C_6H_4NC)_5][ClO_4]$	2216	49
			2155	

supported complex	observed ν_{NC} cm^{-1}	"model" complex	observed ν_{NC} cm^{-1}	reference
$CuCl_2.2H_2O$	2180	$[Cu(CNBu^t)_2(H_4O)_2][ClO_4]_2$	2233	9
		$[Cu(CNBu^t)_4][ClO_4]$	2181	9
		$CuCl(CNp\text{-}MeOC_6H_4)_2$	2141	34
		$CuCl(CNCH_2SO_2C_6H_4CH_3)_2$	2193	10
			2152	
$HAuCl_4.3H_2O$	2250	$AuCl(CNCH_2Ph)$	2265	35
		$[Au(CNCy)_2][ClO_4]$	2250	35
		$[Au(CNCH_2SO_2C_6H_4CH_3)_2]Cl$	2246	10
		AuCl(CNMe)	2271	14
$Pt(cod)_2$	2150	$Pt_3(CNBu^t)_6$	2155	58
$Pd(dba)_2$	2197(s)	$Pd_3(CNBu^t)_6$	2108	61
	2267(sh)		1700	
		"$Pd(CNMe)_2$"	2185	19
$[Rh(cod)Cl]_2$	2130(sh)	$[(CNBu^t)_2RhCl]_2$	2230	52
	2165(s)			
	2197(sh)	RhCl(2,6-xylyl NC)$_3$	2145	54
			2105	

supported complex	observed ν_{NC} cm^{-1}	"model" complex	observed ν_{NC} cm^{-1}	reference
$[Rh(CO)_2Cl]_2$	2197(s)	cis-$Rh(CO)_2(CNBu^t)Cl$	2223	56
	2100(w)*		2101*	
	2008(s)*		2033*	
		trans-$Rh(CO)(CNBu^t)_2Cl$	2181	56
			2011*	
		$[Rh(CNBu^t)_4]Cl$	2167	56

* CO vibration

Table 2.

metal complex	postulated complexation reaction	analytical figures (mmol g^{-1}) Calculated M	Calculated Cl or P	Found M	Found Cl or P
$RhCl_3.XH_2O$	$RhCl_3.XH_2O + 2CNR \rightarrow$				
	$RhCl_3(CNR)_2(H_2O) + (X-1)H_2O$	0.26	0.78	0.28	0.99
K_2PtCl_4	$K_2PtCl_4 + 2CNR \rightarrow$				
	$PtCl_2(CNR)_2 + 2KCl$	0.40	0.80	0.41	0.79
$Na_2PdCl_4.3H_2O$	$2Na_2PdCl_4 + 2CNR \rightarrow$				
	$Pd_2Cl_4(CNR)_2 + 4NaCl$	0.85	1.70	0.95	1.44
$AgNO_3$	$AgNO_3 + 2CNR \rightarrow$				
	$Ag(CNR)_2NO_3$	0.47	-	0.59	-
$AgPF_6$	$AgPF_6 + 2CNR \rightarrow$				
	$Ag(CNR)_2PF_6$	0.40	0.40	0.40	0.35
$HgCl_2$	$HgCl_2 + 1.7\ CNR \rightarrow$				
	$0.7\ HgCl_2(CNR)_2 + 0.3\ HgCl_2(CNR)$	0.56	1.12	0.57	1.12
$CoCl_2$	$CoCl_2 + 2CNR \rightarrow$				
	$CoCl_2(CNR)_2$	0.48	0.96	0.48	1.07
$FeCl_2$	$FeCl_2 + 2CNR \rightarrow$				
	$FeCl_2(CNR)_2$	0.48	0.96	0.50	1.24
$CuCl_2.2H_2O$	$2CuCl_2 + 5RNC + 2H_2O \rightarrow$				
	$2CuCl(CNR)_2 + HCl + CO_2 + RNH_3Cl$	0.40	0.60	0.30	0.54
$HAuCl_4.3H_2O$	$HAuCl_4 + 2H_2O + 2RNC \rightarrow$				
	$AuCl(CNR) + CO_2 + 2HCl + RNH_3Cl$	0.45	0.90	0.49	0.90

Table 2 Continued

$Pt(cod)_2$	$Pt(cod)_2$ + CNR →				
	$Pt(CNR)$ + 2cod	0.86	-	0.71	-
$Ni(cod)_2$	$Ni(cod)_2$ + CNR →	0.97	-	1.07	-
	$Ni(CNR)$ + 2cod	0.94*			
$Pd(dba)_2$	$Pd(dba)_2$ + 2CNR →				
	$Pd(CNR)_2$ + 2dba	0.49	-	0.54	-
$[(cod)RhCl]_2$	$[(cod)RhCl]_2$ + 4CNR →				
	$(cod)RhCl(CNR)$ + $RhCl(CNR)_3$ + cod	0.47	0.47	0.56	0.70
$[Rh(CO)_2Cl]_2$	$[Rh(CO)_2Cl]_2$ + 3RNC →				
	$Rh(CO)_2(CNR)Cl$ + $Rh(CO)(CNR)_2Cl$ + CO	0.61	0.61	0.69	0.86

* calculated figure assuming oxidation to NiO(OCNR)

and analytical data allow reasonable deductions to be made regarding the nature of the supported species.

Three general points can be made:

(i) in no case are more than two isocyanide groups co-ordinated to a single metal atom;

(ii) the tendency towards metal reduction is diminished on the polymer compared to homogeneous solution;

(iii) there is a large variation in the rates of complexation of the different metal salts.

As the polymer supported isocyanide can be considered as RCH_2NC, it is, as such, an alkyl isocyanide and so comparisons of the polymer-supported complexes with those of monomeric isocyanides will be limited to alkyl compounds (where these exist.)

(See Tables 1 & 2)

(a) Platinum(II), Palladium(II) and Nickel(II).

Compounds of the type $[PtX_2(RNC)_2]$, (X=Cl, Br, NO_2, CN, R=alkyl or aryl), are among the first reported platinum(II)-isocyanide complexes[16,17], although early work was concerned primarily with aryl isocyanide reactions.

Platinum and palladium complexes of the formula $[M(CNCH_3)_4]^{2+}$ are isolated as the hexafluorophosphate or tetrafluoroborate salts from the reaction of excess methyl isocyanide with the aqueous solution of the appropriate MCl_4^{2-} salt[18]. A different product, $[(CH_3NC)_6Pd_2][PF_6]_2$, can be obtained by allowing the reaction solution to stand before addition of the precipitant. The authors suggest that this reduction to Pd(I) occurs via oxidation and hydrolysis of a methyl isocyanide ligand as shown in the reaction scheme overleaf[19].

$$[(CH_3NC)_4Pd]^{2+} + H_2O \longrightarrow [(CH_3NC)_3PdC(O)NHCH_3]^{+} + H^{+}$$

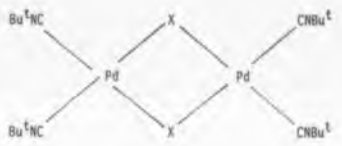
$$\downarrow + H_2O$$

$$[(CH_3NC)_3Pd] + H^{+} + CO_2 + CH_3NH_2$$

$$\downarrow + [(CH_3NC)_4Pd]^{2+}$$

$$[(CH_3NC)_6Pd_2]^{2+} + CH_3NC$$

The intermediate $[(CH_3NC)_3PdC(O)NHCH_3]^{+}$ can also be isolated as the hexafluorophosphate salt. The preparation of the platinum dimer follows a similar course (tetrafluoroborate used as precipitant). Palladium(I) dimers may also be prepared by the reaction of $[Pd(CNBu^t)_2]_3$ with $Pd(CNBu^t)_2X_2$ (X=Cl, Br, I) to yield $[Pd(CNBu^t)_2X]_2$ for which a dimeric structure,as shown, has been suggested[15]. (ν_{NC} 2170 cm^{-1}).



The monomeric, thermally and air stable $PdX_2(CNR)_2$ was also prepared by reaction of the appropriate palladium halide with excess t-butyl isocyanide. This complex had isocyanide infrared bands at higher frequency (around 2230 cm^{-1}) as expected for a higher oxidation state metal.

For platinum salts of the type $[Pt(CNR)_4][PtCl_4]$, (R= p-tolyl, p-anisyl or cyclohexyl), the complexes are transformed into their cis-$Pt(CNR)_2Cl_2$) isomers on refluxing in chloroform solution[20].

For the polymer-supported platinum complex the analytical data (table 2) and infrared spectrum (figure 2, and table 1) are consistent with the formulation as neutral, monomeric $PtCl_2(CNR)_2$. From the infrared figures, the "model" complex $[NBu^n_4][PtCl_3(CNMe)]$ (2240 cm^{-1}) has the closest agreement with the supported complex (2222 cm^{-1}). However the analytical figures give very good agreement for a platinum:isocyanide ratio of 1:2. It should be noted that there is often a variation of around $\pm$ 10 cm^{-1} in the figures quoted by different authors for the same complex, as well as differences in figures quoted for the free isocyanide ligand. For example:

ligand/complex	$\bar{\nu}_{CN}$ (cm^{-1})	
CH_3NC	2170	8
CH_3NC	2158	21
Bu^tNC	2131	9
Bu^tNC	2143	21
$Co(C_6H_5NC)_5(ClO_4)_2$	2190(m),2220(s)	22
$Co(C_6H_5NC)_5(ClO4)_2$	2184(s),2209(vs),2236(sh,w)	33

Some variation may also be expected since the polymer-supported isocyanide is a "benzyl" isocyanide rather than a pure alkyl isocyanide. Due to the broadness of the bands, the precision of the wavenumber measurements used in this work is estimated to be approximately $\pm$ 5 cm^{-1}. Thus, if the infrared isocyanide stretching frequency for the polymer-supported complex is within 20 cm^{-1} of the appropriate "model" compound, reasonably confident deductions regarding the structure of the supported complex can be made.

The single infrared band observed in the spectrum of the polymer-supported isocyanide-platinum complex (figure 2) suggests a trans geometry, in contrast to the monomeric platinum-isocyanide complexes of structure $Pt(CNR)_2Cl_2$ which are commonly cis, (R=CH_3[14], C_6H_5[24] etc.). The broadness of the band may, however, obscure the doublet expected for cis-geometry. In a spectroscopic study of methyl isocyanide complexes of platinum(II), Goodfellow et al[14] recorded the infrared spectrum of cis-$[PtCl_2(Cl_2(CNCH_3)_2]$ with two bands at 2281 and 2253 cm respectively, but also list two bands for trans-$[PtI_2(CNCH_3)_2]$, at 2268 and 2248 cm^{-1} respectively. Two bands are also listed for the corresponding palladium complexes. The stereochemistry of the polymer-supported platinum complex is therefore uncertain.

In the case of the supported palladium complex, the infrared isocyanide stretching band is at 2260 cm^{-1} (figure 3) and the analytical data show a 1:1 palladium:isocyanide ratio. From a comparison with similar "model" compounds (table 1), it is obvious that reduction to palladium(I) (2166 cm^{-1}) has not taken place. The value for the isocyanide band for cis-$PdCl_2(CNCH_3)_2$, at 2280 cm^{-1} [14], is close to that for the supported complex as is the value[25] for the complex $[PdCl_2(CNp\text{-}tolyl))]_2$, at 2220 cm^{-1}, if about 50 cm^{-1} is added to compensate for the aryl nature of the isocyanide. Therefore the product from the reaction of the polymer-supported isocyanide with sodium tetrachloropalladate(II) seems best formulated as the dimer $PdCl_2(CNR)_2(\mu\text{-}Cl)_2$. Dimers of this type have been isolated from the reaction of $PdCl_2(MeCN)_2$ with $PdCl_2(CNR)_2$, (R = C_6H_4 or p-MeC_6H_4).[25] A recent report of another supported isocyanide-palladium(II) complex, (using an acrylamide based support) also has a palladium:isocyanide ratio of approximately 1:1.[2]

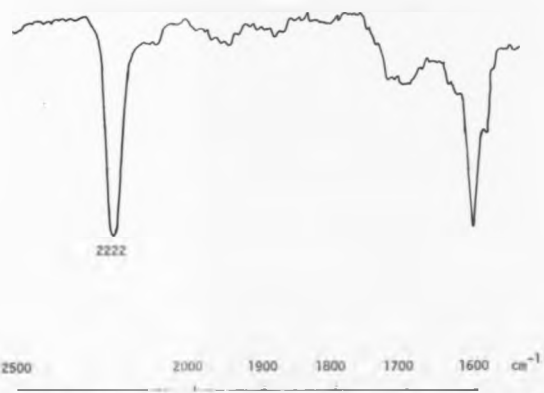


Figure 2. I.R. spectrum of the product from the reaction of K_2PtCl_4 with the polymer-supported isocyanide.

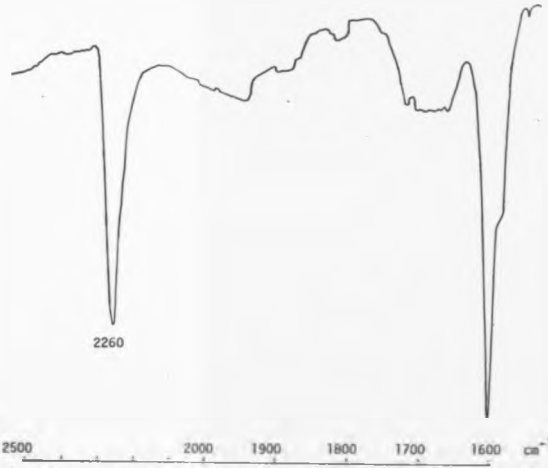
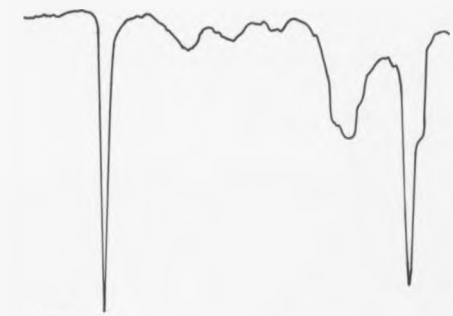


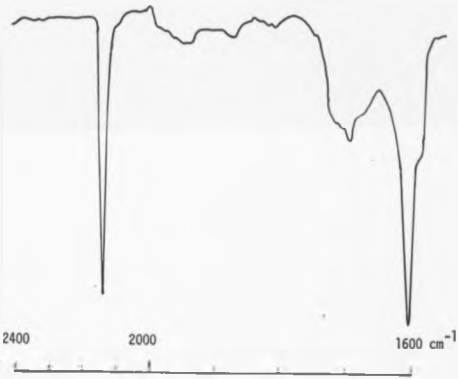
Figure 3. I.R. spectrum of the product from the reaction of Na_2PdCl_4 with the polymer-supported isocyanide.

Although Malatesta[26] claims a lively and very exothermic reaction takes place between isocyanides and alcoholic solutions of nickel(II) salts, the products were ill-defined and few other nickel(II) - isocyanide complexes have been reported. In a 1983 review, only one such complex, $[Ni(CNBu^t)_4][ClO_4]_2$ is mentioned.[27] This scarcity of complexes may be a consequence of the high catalytic activity of nickel compounds for isocyanide polymerization.

Using our polymer, attempts to complex nickel(II) from aqueous tetrahydrofuran solutions of $NiCl_2.6H_2O$ or from anhydrous tetrahydrofuran solutions of $NiCl_2$ yielded only unreacted polymer. Although similar reactions (using the acrylamide based isocyanide polymer) have been reported to lead to the polymerization of the isocyanide group, when an excess of the isocyanide was used[1], no detectable change in the intensity of the isocyanide stretching vibration was observed in our polymer-supported reaction, (figure 4). Also, the isocyanide-specific titration (chapter 2, section 5.5) showed little change between the polymer before and after the attempted complexation of Ni(II). (Before:0.90 mmol g^{-1}, after:0.84 mmol g^{-1}). There is also no infrared evidence for the formation of the poly(iminomethylene) product, $[R - N = C\lesssim]_n$ which would be expected to show an isocyanide band around 1700 cm^{-1}. A study of the nickel(II)-catalysed polymerization of isocyanides[28] found that an excess of isocyanide was necessary for the production of such polymers; therefore, as our polymer-supported isocyanide complexation experiments were performed with an excess of the metal salt, such polymerization may be unlikely.



(a) $NiCl_2.6H_2O$



(b) $NiCl_2$

Figure 4. I.R. spectrum of the product from the reaction of nickel salts with the polymer-supported isocyanide.

(b) Rhodium(III)

Complexes of the type $[Rh^{I}(RNC)_4]X$ $(X=BF_4)$ may be prepared from the reaction of rhodium(III) trichloride with an excess of methyl isocyanide[29], though an intermediate Rh(III) complex $[RhI_3(CNCH_3)_3]$ may be isolated by addition of sodium iodide to the yellow solution formed initially (hence complexation occurs before reduction). The cation $[Rh(CNR)_4]^+$ is easily oxidized, reacting rapidly with iodine in chloroform to yield the $[Rh(CNR)_4I_2]^+$ salt, $(R=CH_3)$[30].

The polymer-supported complex is best formulated as $RhCl_3(CNR)_2(H_2O)$ from the analytical data - one molecule of water is included to maintain octahedral co-ordination, although this cannot be determined directly from the analytical data. The supported complex has an infrared isocyanide stretching frequency at 2214 cm^{-1} (figure 5) which is not consistent with reduction to rhodium(I), 2197 cm^{-1}). Also there is no evidence of oxidation products for the isocyanide (see later section (c)) which may be expected if reduction of the rhodium had occurred. The "model compound" $Rh(CNCH_3)_3I_3$ has a figure of 2243 cm^{-1} for the infrared isocyanide band, and is closest to the value of 2214 cm^{-1} for the supported complex. As stated before, increasing the number of isocyanide ligands tends to increase the infrared stretching frequency of the isocyanide, therefore the formulation of the complex as unreduced $RhCl_3(CNR)_2(H_2O)$ seems reasonable from both the infrared and analytical data. The infrared band seen for this supported complex is similar to the results obtained by Arshady and Corain[2], who suggested a formula of (P)-$[(NC)_2$-$RhCl_3(H_2O)]$ for the product of the reaction between hydrated rhodium trichloride and their acrylamide based polymer-supported isocyanide, (2240 cm^{-1} (nujol)).

These results emphasise the differences observed between monomeric isocyanides in solution and the polymer-supported species, as reduction to rhodium(I) is commonly observed for the solution reaction of rhodium(III)

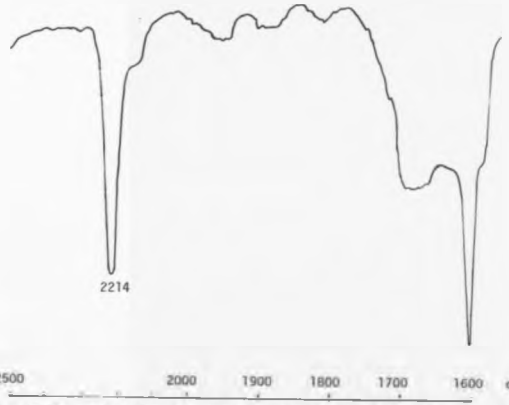


Figure 5. I.R. spectrum of the product from the reaction of $RhCl_3.xH_2O$ with the polymer-supported isocyanide.

with monomeric isocyanides, but no such reduction is observed for the polymer-supported species.

(c) Copper(II), Silver(I) and Gold(III)

The reaction of silver(I) salts with aryl and and alkyl isocyanides is known to give complexes of the stoichiometry $[Ag(CNR)_2X]$ and $[Ag(CNR)_4X]$ $(X=ClO_4, NO_3, PF_6, BF_4.)$[10,11,31] The reaction of silver tetrafluoroborate with p-toluenesulphonylmethyl isocyanide (L) yielded L_2AgBF_4[10], having an infrared isocyanide stretching frequency of 2230 cm^{-1}. More recently some compounds involving very bulky isocyanide ligands have been reported[32] such as the di-coordinate species $[Ag(CNR)_2(PF_6)]$ $(R=2,4\text{-}Bu^t_2\text{-}6\text{-}CH_3\text{-}C_6H_2,\ 2,4,6\text{-}Bu^t_3C_6H_2,\ 2,6\text{-}(CH_3)_2C_6H_3,)$ and the tri-coordinate species $[Ag(CNR)_3(PF_6)]$ $(R=2,4,\text{-}Bu^t_2\text{-}6\text{-}CH_3\text{-}C_6H_2$ or $2,6\text{-}(CH_3)_2C_6H_3,)$. An x-ray crystal structure determination of $[Ag(CNC_6H_2Bu^t_3)_2(PF_6)]$ shows a highly distorted tetrahedral species resulting from the co-ordination of a bidentate hexafluorophosphate ligand.

For our polymer-supported species, very good agreement is found for experimental and calculated analysis figures (see table 1) for the silver hexafluorophosphate-isocyanide complex, formulated as $Ag(CNR)_2PF_6$. For the corresponding silver nitrate complex the agreement is not as good, but the data is most consistent with the formulation of the complex as $Ag(CNR)_2NO_3$. The isocyanide bands in the infrared spectra of the two supported complexes are similar, (figures 6 and 7), 2220 cm^{-1} for the nitrate and 2238 cm^{-1} for the hexafluorophosphate, and although these figures are slightly higher than those of most of the "model" compounds quoted (table 1)

i.e. $[Ag(CNC_6H_{11})_2]ClO_4$ 2215,2190 cm^{-1}, 33

$[Ag(CNC_6H_{11})_4]ClO_4$ 2182,2150 cm^{-1}, 33

they are in good agreement with the figure for $[Ag(CNCH_2SO_2C_6H_4CH_3)_2]BF_4$ at 2230 cm^{-1}. 10

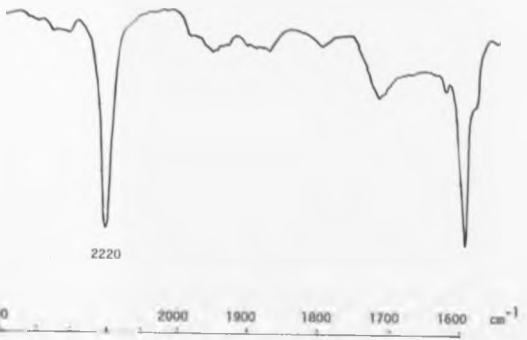


Figure 6. I.R. spectrum of the product from the reaction of $AgNO_3$ with the polymer-supported isocyanide.

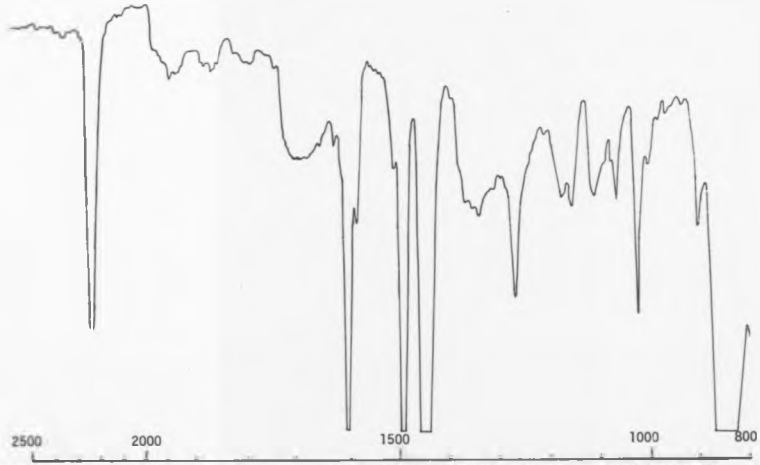


Figure 7. I.R. spectrum of the product from the reaction of $AgPF_6$ with the polymer-supported isocyanide.

Although the copper(II)-isocyanide complexes have been prepared, they are unstable with respect to reduction to copper(I). Stephany and Drenth[9] synthesized $[Cu(CNR)_4(H_2O)_2]X_2$ (R=Bu^t, 1,1,3,3-tetramethylbutyl ; X=ClO_4,BF_4) but found that the complexes decomposed rapidly to yield the appropriate copper(I) derivative $[Cu(CNR)_4]X$. The infrared spectrum of the copper(II) complexes showed an isocyanide band in the region 2230-2245 cm^{-1}, moving to 2181 cm^{-1} on reduction to the copper(I) complex. The reaction of copper(I) halides with aryl isocyanides yields a series of $CuX(CNR)_y$ complexes [31,34], (R=phenyl,p-tolyl,p-anisyl; X=Cl,Br; y=1-4), where y is dependant on both CNR and X.

The infrared spectrum of the supported complex (figure 8) shows a single absorption at 2180cm^{-1} which is similar to the values obtained for the other copper(I)-isocyanide "model" compounds (see table 1) which have isocyanide bands from 2152-2193 cm^{-1}, but inconsistent with the value 2233 cm^{-1} for the copper(II)-isocyanide complex. Note also that the aryl example quoted, $CuCl(CNp\text{-}CH_3OC_6H_4)_2$, which has an infrared isocyanide absorption at 2141 cm^{-1} is also in the same range when approximately 50 cm^{-1} is added to compensate for the aryl nature of the ligand.

It would seem likely therefore that the reaction of the polymer-supported isocyanide with copper(II) chloride proceeds with concomitant metal reduction and complexation. Although the oxidation products of the isocyanide in homogeneous solution have not generally been well characterised, the half-cell can probably be regarded as the sequence of reactions:

(1) $2RNC + 2H_2O \rightarrow 2RNCO + 4H^+ + 4e^-$

(2) $RNCO + H_2O \rightarrow RNH_2 + CO_2$

(3) $RNH_2 + RNCO \rightarrow (RNH)_2CO$

Figure 8. I.R. spectrum of the product from the reaction of $CuCl_2.2H_2O$ with the polymer-supported isocyanide.

OVERALL:

(4) $2RNC + 3H_2O \rightarrow CO_2 + (RNH)_2CO + 4H^+ + 4e^-$

The isocyanide is oxidised to isocyanate, followed by hydrolysis and condensation to yield the symmetrical urea. Due to the low loading of isocyanide on the polymer support (and any possible mobility restrictions), reaction (3) seems unlikely to occur on the polymer-supported species; therefore the most likely half-cell becomes:

(5) $RNC + 2H_2O \longrightarrow RNH_3^+ + H^+ + CO_2 + 2e^-$

In the case of the copper(II) $\longrightarrow$ copper(I) reduction, chlorine will be retained on the polymer both as $CuCl(CNR)_2$ and RNH_3Cl. The infrared spectra (KBr discs) recorded always contained a broad absorption above 3100 cm^{-1}, assumed to be due to moisture absorbed during sample preparation; thus the presence of $[RNH_3]Cl$ cannot be detected in the spectrum. However there is no trace of isocyanate (2250-2275 cm^{-1}) or urea (1660 cm^{-1}) absorptions in the spectrum. Calculations based on a reaction equation as indicated below give good agreement with the experimental analysis figures:

$2CuCl_2 + 5RNC + 2H_2O \longrightarrow 2CuCl(CNR)_2 + HCl + CO_2 + RNH_3Cl$

Analytical figures, (mmol g^{-1}):

Metal	Chlorine	
0.40	0.60	Calculated
0.30	0.54	Found

In the reaction of $Cu(NO_3)_2.6H_2O$ with an acrylamide based polymer-supported isocyanide, the product exhibits an infrared isocyanide band at 2195 cm^{-1}, as does the product when $Cu(acac)_2$ is used. Although the isocyanide content of the resin is quoted (2.6 mmol g^{-1}) and also a figure for the metal content (1.9%), no other attempt is made by the authors to determine the nature of the supported complex[1].

Complexes of the type (RNC)AuCl have been prepared by the two methods described below by Bonati and Minghetti[35], who state that the reaction of tetrachloroauric(III) acid with excess isocyanide in hot alcohol gives a crystalline compound but only in poor yield, according to the following equation:

$$[H_3O][AuCl_4] + 2RNC \longrightarrow (RNC)AuCl + 3HCl + RNCO$$

The authors favour the preparation of the gold(I)isocyanide complex by displacement of dimethylsulphide from $(CH_3)_2SAuCl$;

$$RNC + (CH_3)_2SAuCl \longrightarrow (RNC)AuCl + (CH_3)_2S \qquad (R=alkyl\ or\ aryl)$$

Although earlier work by Sacco and Freni[36] reported the isolation of gold (III)-isocyanide complexes, $(RNC)AuCl_3$ (R=p-methoxyphenyl, p-tolyl), later work quotes only reduction to gold(I). These reactions were performed with an excess of isocyanide and yielded complexes of stoichiometry AuCl(CNR) and $[Au(CNR)_2]X$ (X=perchlorate, tetrafluoroborate; R=aryl or alkyl).

All of the "model" compounds listed in table 1 are gold(I)-isocyanide compounds, no infrared data being available for the gold(III) complexes proposed in early work. The isocyanide stretching vibrations for

$[Au(CNCy)_2]ClO_4$ at 2250 cm^{-1}, and for $[Au(p\text{-}CH_3C_6H_4SO_2CH_2NC)_2]ClO_4$ at 2246 cm^{-1} are very close to the value observed for our polymer-supported isocyanide-gold complex (2250 cm^{-1}), (figure 9). However the supported complex has a gold:isocyanide ratio of 1:1 from the analytical data (which takes into account the reduction of Au(III) to Au(I) and the infrared isocyanide stretching frequency is within 20 cm^{-1} of the examples quoted for the same gold:isocyanide ratio:

$AuCl(CNCH_2C_6H_5)$ 2265 cm^{-1}

$AuCl(CNCH_3)$ 2271 cm^{-1}

Therefore the reaction between the polymer-supported isocyanide and tetrachloroauric(III) acid is best represented by reduction, followed by complexation as AuCl(CNR) as outlined in the equation below:

$$HAuCl_4 + 2H_2O + 2RNC \longrightarrow AuCl(CNR) + CO_2 + 2HCl + RNH_3Cl$$

(d) Zinc(II), Cadmium(II) and Mercury(II)

Although isocyanide complexes of the type $(RNC)_2ZnX_2$ were prepared by Sacco[37] (R=p-tolyl and X=chloride, bromide or iodide), the results obtained for the reaction of zinc chloride with polymer-supported isocyanide are more in agreement with Malatesta[26], who stated that isocyanides have a very low affinity for zinc. Though the recovered polymer from the reaction with zinc chloride exhibits a pink colour, (previously light yellow-brown), the metal incorporation is negligible from the analysis (0.015mmolg^{-1}, 0.1% zinc) and the infrared spectrum shows only the isocyanide stretching frequency of the starting polymer (figure 10a).

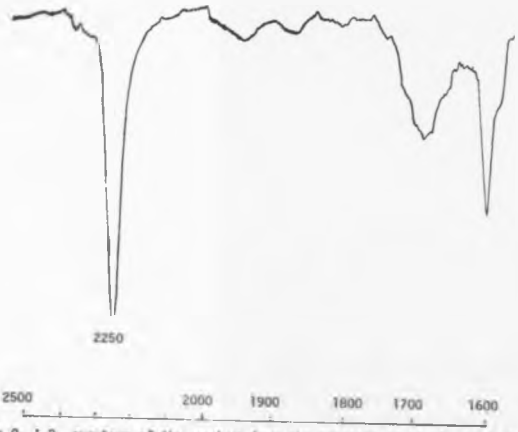


Figure 9. I.R. spectrum of the product from the reaction of $HAuCl_4.3H_2O$ with the polymer-supported isocyanide.

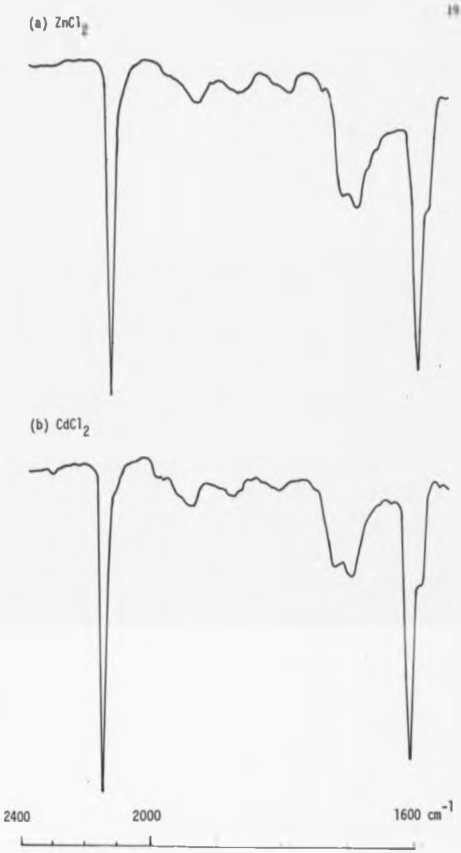


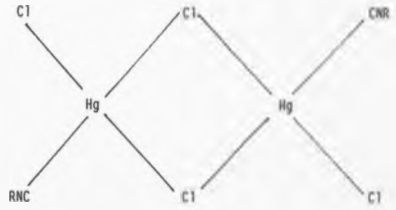
Figure 10. I.R. spectra of the products from the reaction of (a) $ZnCl_2$ and (b) $CdCl_2$.

The case of cadmium is similar; Sacco and Freni[36] prepared $(RNC)CdX_2$ (R=p-tolyl and X=chloride or bromide) but the infrared spectrum for the product for the polymer-supported isocyanide-cadmium chloride reaction again showed only the isocyanide stretching frequency of the starting material (figure 10b).

The reaction of mercury(II) salts with isocyanides resulting in the reduction of the metal was reported as early as 1884. In later work, Klages and Monkmeyer[31] proposed the following equation for the reaction of excess p-tolyl isocyanide with mercury(II) chloride:

$$4HgCl_2 + 2ArNC + 3H_2O \longrightarrow 4HgCl + CO_2 + (ArNH)_2CO + 4HCl$$

A complex of the stoichiometry $Hg(CNR)_2Cl_2$ was also reported as a product from this reaction. This reduction was also observed by Sawai and Takizawa[39] in the reaction between phenyl or t-butyl isocyanide with mercury(II) chloride in the presence of water; the products isolated were mercury(I) chloride and a small amount of the corresponding urea. The reaction between mercury(II) chloride and excess t-butyl or 2,6-dimethylphenyl isocyanide in cold ether[40] yielded the complex $HgCl_2CNR$ for which the authors propose the following dimeric structure:



The t-butyl isocyanide-mercury complex exhibits an isocyanide stretching band at 2245 cm^{-1} in the infrared spectrum, whilst the band is at the lower frequency of 2218 cm^{-1} for the 2,6-dimethylphenyl isocyanide-mercury complex, as would be expected due to the differences between the isocyanide stretching vibrations observed for alkyl and aryl isocyanides. Oligomers and low molecular weight polymers were produced on heating mercury(II) chloride with benzyl, cyclohexyl or 2,6-xylyl isocyanides in dry tetrahydrofuran[41], the first two isocyanides polymerizing more readily. It should be noted also that no mercury(I)-isocyanide complexes are isolated.

The structure of the polymer-supported isocyanide-mercury complex is unclear. The analysis shows a mercury content of 0.57 mmol g^{-1} and chlorine content of 1.12 mmol g^{-1}. Calculations made assuming no reduction of mercury give the following results:

$HgCl_2 + 2\ RNC \longrightarrow HgCl_2(CNR)_2$

Hg content : 0.45 mmol g^{-1}

Cl content : 0.90 mmol g^{-1}

$HgCl_2 + RNC \longrightarrow HgCl_2(CNR)$

Hg content : 0.80 mmol g^{-1}

Cl content : 1.60 mmol g^{-1}

As the experimentally determined figures fall between these two sets of figures it is possible that a mixture of the two complexes is present. Calculations for 0.7 $HgCl_2(CNR)_2$ and 0.3 $HgCl_2(CNR)$ give figures which are

in very good agreement (Hg : 0.56 mmol g^{-1}, Cl : 1.12 mmol g^{-1}) with those found by analysis. However, the infrared spectrum for the supported complex (figure 11) shows some evidence of polymerization of the isocyanide, having a broad absorption band at around 1690 cm^{-1}, as well as a band at around 2350 cm^{-1} as a shoulder on the complexed isocyanide band at 2265 cm^{-1}. A weak band at around 1700 cm^{-1} is usually found in the spectra of the polymer-supported isocyanides, and is presumed to arise from a small amount of polymerization which occurs in the generation of the isocyanide group. In the spectrum of the supported mercury complex however, the band is broader and more intense; indicating that further polymerization of the isocyanide group may have taken place on reaction with $HgCl_2$. It should be noticed from the infrared spectrum (figure 11) that the complexed isocyanide band is relatively less intense than similar complexed isocyanide bands for other metal-isocyanide complexes (see figures 2-9 for comparison). If some of the isocyanide is being polymerized by the mercury(II) chloride substantially less free isocyanide will remain available for complexation. Calculations indicate that if 0.66 mmol g^{-1} of isocyanide remain unpolymerized and react to yield a complex $HgCl_2$(CNR), the mercury content would be 0.56 mmol g^{-1} (analysis figure : 0.57 mmol g^{-1}) and the chlorine content would be 1.12 mmol g^{-1} (analysis figure : 1.12 mmol g^{-1}). A reaction of this nature may therefore have occurred.

Other possible explanations include the reduction of the mercury(II) to mercury(I) with corresponding oxidation of the isocyanide, which occurs in the reactions of monomeric isocyanides in solution, to yield the appropriate isocyanate, and subsequently the symmetrical urea. The latter compound may be expected to have a carbonyl stretching frequency in the vicinity of 1660 cm^{-1}, somewhat lower than the band observed in the spectrum of the polymer-supported product and as stated earlier, is not likely to occur on a polymer support. The isocyanate would be expected to

Figure 11. I.R. spectrum of product from the reaction of $HgCl_2$ with the polymer-supported isocyanide.

exhibit a stretching vibration at 2250-2275 cm^{-1}, which is considerably lower than the frequency observed for the broad shoulder on the complexed isocyanide band in the spectrum of the polymer-supported isocyanide-mercury complex. It should also be noted that no evidence for the formation of isocyanates as oxidation products is observed in the spectra of those polymer-supported isocyanide-metal complexes which have been found to undergo metal reduction and therefore it is unlikely that this case should be different.

Sawai, Takizawa and Itaka[42] report that $HgCl_2$ undergoes transalkylation in the presence of t-butyl isocyanide, to yield $Hg(CN)_2$. This, if formed during the polymer supported isocyanide reaction, may precipitate in the aqueous tetrahydrofuran reaction medium and therefore some or all may remain trapped in the polymer matrix and could be detected by its cyanide stretching vibration in the infrared spectrum. However, $Hg(CN)_2$ has its cyanide stretching band at 2195 cm^{-1} and therefore does not account for the shoulder observed at 2350 cm^{-1}.

It is possible that a mercury-isocyanide complex is first formed on the polymer, and that some of the latter then isomerises to the corresponding mercury-nitrile complex, which would give rise to a complex-nitrile vibration in the spectrum. Free nitriles have their infrared CN stretch at around 2250 cm^{-1} and an increase of +100 cm^{-1} would seem feasible for the complexed CN stretch, (as the free isocyanide band is found to increase by up to 150 cm^{-1} on complexation). With the limited analytical and infrared data available for the polymer-supported complex, it is therefore difficult to determine which of the following (or which combination) is the true representation of the results found:

(i) Polymerization of the isocyanide, with complexation of remainder as $HgCl_2(CNR)$

(ii) Complexation of a mixture of $HgCl_2(CNR)$ and $HgCl_2(CNR)_2$

(iii) Complexation of $HgCl_2$ with isocyanide, with some isomerization to Hg-nitrile (retained on polymer).

(iv) Any combination of these.

(3) Rates of complexation from aqueous tetrahydrofuran.

Although kinetic data for homogeneous solution reactions are not available, complexation by the polymer-supported isocyanide appears to proceed much more slowly in the case of complexation of normal oxidation state metal salts from aqueous tetrahydrofuran. Greatly differing rates of complexation were observed for the following complexes:

$HAuCl_4$, K_2PtCl_4, $AgPF_6$, $RhCl_3.xH_2O$,

ranging from 98% complete complexation in two hours for $HAuCl_4$, to several days for complete complexation of $RhCl_3.xH_2O$.

It was found that the rate of complexation could be accelerated by use of ultrasound; in the case of the complexation of $RhCl_3.xH_2O$, the reaction time is reduced to 24 hours. These rates were determined from a quantitative analysis of the infrared spectra of samples removed at regular time intervals until complete complexation occurred. (See experimental section for details). The rates were determined for both 9% and 2%

crosslinked polymer-supported isocyanide resins, to determine the effect of decreasing the crosslink ratio, thus increasing the swelling capacity of the resin. (Rate graphs - figures 12-15).

For the 9% crosslinked resin, the rates were found to be in the order Rh<<Pd<Ag<Pt<<Au. Although generally the rates were found to be slightly faster for the 2% crosslinked resin, with the exception of silver, the rates were very similar for both 2% and 9% crosslinked polymers. In the case of silver, the rate of complexation was considerably faster for the 2% crosslinked resin, thus the order becomes:
Rh<<Pd<Pt<Ag (Au not used). With the possible exception of silver, the differing rates of complexation do not appear to be a result of differing rates of diffusion into the resins, as the metal salts would be expected to diffuse much faster into the considerably more swollen 2% crosslinked resin. In all cases except silver, only a very slight increase is seen between the 9% and 2% crosslinked resin, and this may not be significant since the method of determining the rate of complexation (from the infrared spectrum) is not very precise. It therefore appears that the results reflect kinetic differences in the rate of substitution and therefore may form a basis for metal separation. For example, the polymer recovered from extraction of an equimolar solution of $RhCl_3.xH_2O$ and K_2PtCl_4 under the usual conditions contained >96% platinum, the remaining 4% being rhodium (although the actual experimental figure is so low that considerable error is involved). Thus the polymer exhibits some selectivity in the complexation of these metals.

Figure 12.

Graph of the rate of uptake of metal salt by the polymer-supported isocyanide (i) 2% crosslinked resin,

(ii)9% crosslinked resin,

for K_2PtCl_4.

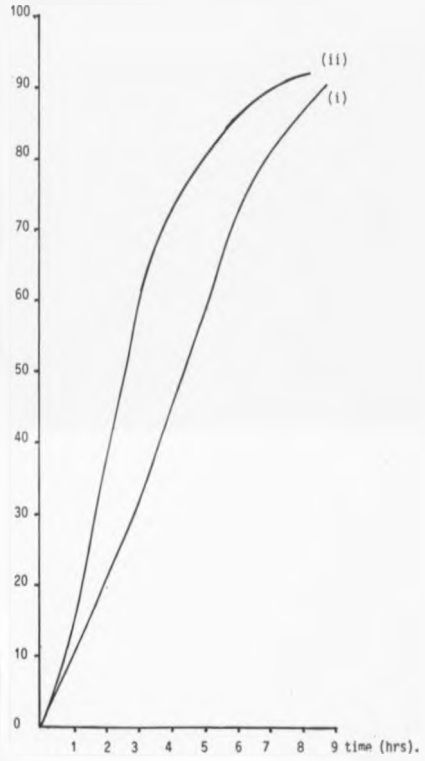


Figure 13.

Graph of the rate of uptake of metals salts by the polymer-supported isocyanide (i) 2% crosslinked resin,
(ii) 9% crosslinked resin,
for $AgPF_6$ and Na_2PdCl_4.

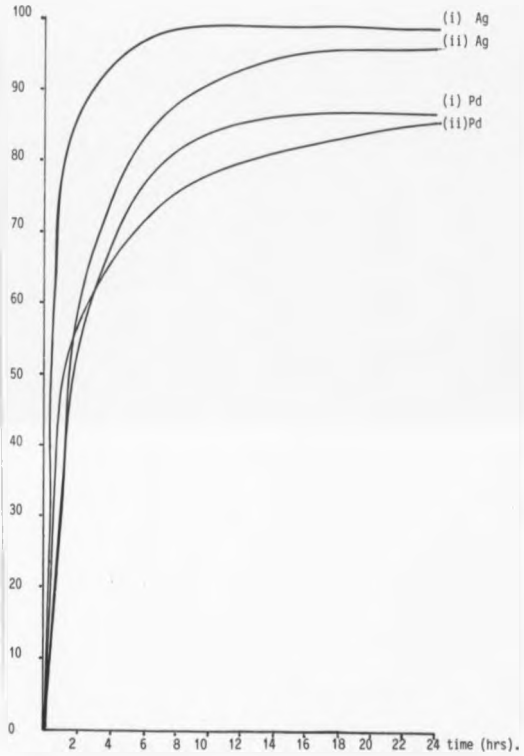


Figure 14.

Graph of the rate of uptake of metal salts by the polymer-supported isocyanide (i) 2% crosslinked resin,
(ii) 9% crosslinked resin,
for $AgPF_6$ and K_2PtCl_4.

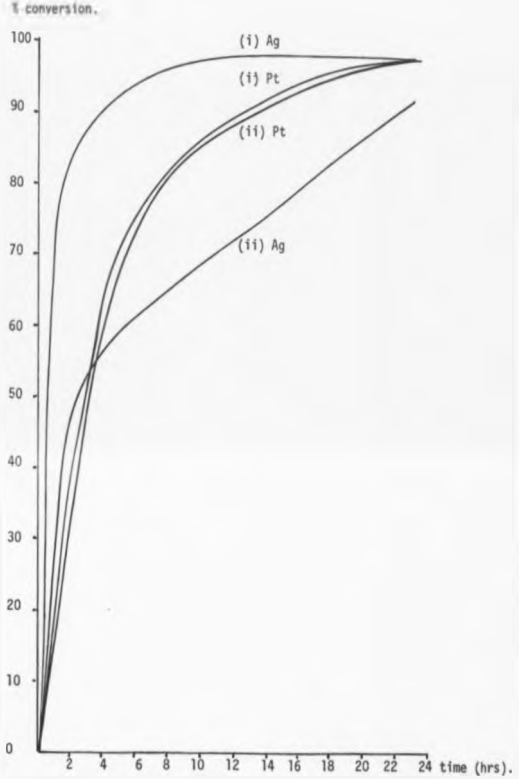
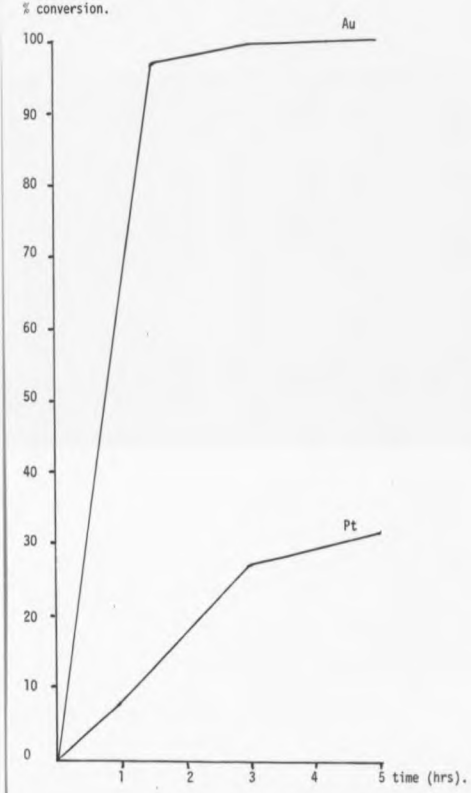


Figure 15.

Graph of the rate of uptake of metal salts by the polymer-supported isocyanide

(ii) 9% crosslinked resin,

for $HAuCl_4.3H_2O$ and K_2PtCl_4.



(4) Attempted extraction of metal from the polymer-supported metal complex

Several attempts were made to remove the rhodium and platinum metal complexes from the polymer-supported isocyanide by extraction with strong donor solvents such as dimethylformamide, dimethylsulphoxide, pyridine and piperidine; in some cases the experiments were carried out in an ultrasonic bath to accelerate the reaction. However, very little success was found with any of these solvents, although a small amount of the rhodium complex was removed by dimethylsulphoxide when the reaction flask was immersed in an ultrasonic bath for 24 hours. This was confirmed by the appearance of slight shoulder at 2140 cm^{-1} in the infrared spectrum of the product corresponding to the NC stretching frequency of free isocyanide. The amount of rhodium chloride lost was determined by ultraviolet analysis of the reaction solution, and was found to be approximately 10%. Piperidine was originally thought to show some success in the removal of the platinum salt from the polymer-supported isocyanide-platinum complex due to the appearance of a very small band on the infrared spectrum at 2140 cm^{-1}, and also there was a slight hint of colour in the reaction solution. However when the experiment was conducted in an ultrasonic bath, to accelerate the reaction, the infrared spectrum of the product (figure 16) showed the complete disappearance of the complexed isocyanide band at 2222cm^{-1}, no free isocyanide (2140 cm^{-1}) but a band at approximately 1550 cm^{-1} had appeared. This is assumed to be due to the presence of a metal carbene from the reaction of the metal-isocyanide complex with the amine, according to the scheme given overleaf.[27]

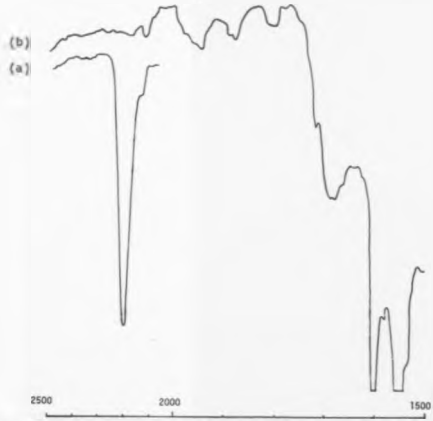
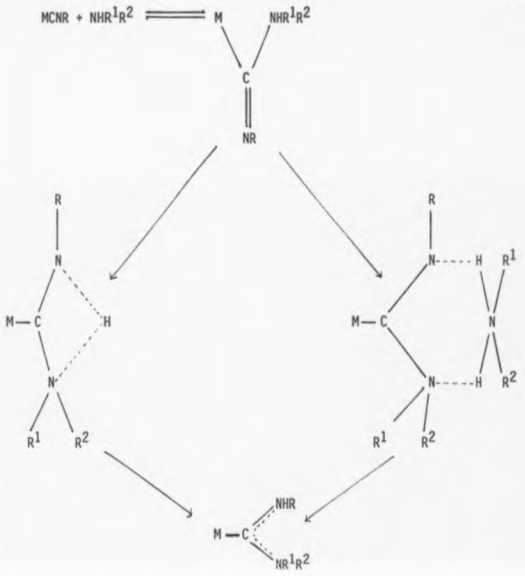
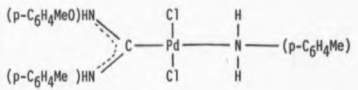


Figure 16. I.R.spectra of the products from the attempted removal of K_2PtCl_4 from the polymer support using piperidine (a) standard technique or (b) ultrasonic technique.



The band at 1550 cm^{-1} is consistent with results obtained for the reaction of $[PdCl_2(CN_p\text{-}C_6H_4OMe)]_2$ with aniline, where the product trans-$PdCl_2\{C(NH\text{-}p\text{-}C_6H_4OMe)NH\text{-}p\text{-}C_6H_4Me\}(NH_2pC_6H_4Me)$ exhibits a <u>carbene</u> CN vibration at 1535(s) cm^{-1} [43].



When the polymer-supported isocyanide-silver hexafluorophosphate complex was swollen in dichloromethane and refluxed for 3 days in the presence of triphenylphosphine, the latter displaced approximately 60% of the complexed silver as estimated from the infrared spectrum (figure 17) which shows both free and complexed isocyanide bands. The reaction solution was evaporated down to leave a solid whose ^{31}P n.m.r. spectrum is shown in figure 18. The two peaks at -2.72 and 27.8 are triphenylphosphine and triphenylphosphine oxide respectively. The peak centered on 144.3 is the PF_6^- anion (septet, J=710Hz). The peak for the $Ag(PPh_3)_4^+$ cation is probably not seen due to its (phosphine) exchange with the free PPh_3.

The limited success obtained with the attempted metal removal reactions indicates that the removal of such complexes from the polymer-support proceeds at a very much slower rate than for similar reactions of monomeric isocyanide-metal complexes in solution. For example, the reaction of $[Ag(CNC_6H_{11})_2]ClO_4$ with triphenylphosphine[33] is carried out in 6 hours at room temperature to yield up to 61% $[Ag(PPh_3)_4]ClO_4$ in contrast to refluxing for 3 days as required in the case of the polymer-supported reaction.

(5) Attempted h.p.l.c. separation of metal salts using the polymer-supported isocyanide.

The polymer-supported isocyanide shows kinetic selectivity in the extraction of metal salts from aqueous tetrahydrofuran under the reaction conditions previously described. However, this extraction occurs at a relatively slow rate - generally 1-2 hours pass before any uptake is observed in the infrared spectrum. Also, the metal complex is bound to the polymer-supported isocyanide quite strongly and cannot easily be removed from from the resin. Therefore any utility of those materials in

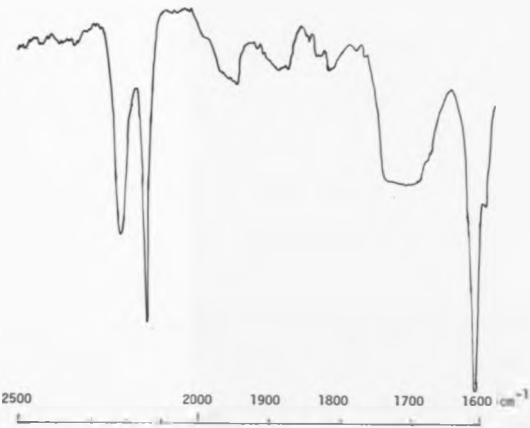
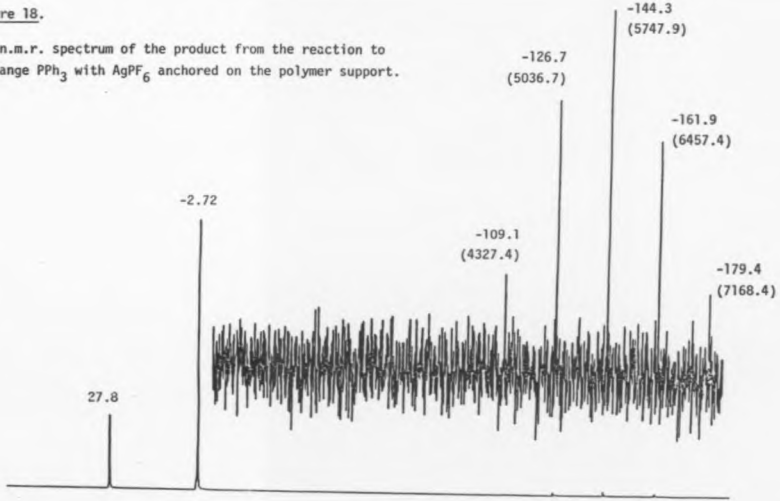


Figure 17. I.R. spectrum of the polymer product from the attempted removal of $AgPF_6$ from the polymer support using PPh_3.

Figure 18.

^{31}P n.m.r. spectrum of the product from the reaction to exchange PPh_3 with $AgPF_6$ anchored on the polymer support.



h.p.l.c. separation would need to rely on a weaker and kinetically more rapid interaction between the metal salt and the isocyanide group. Since the interaction between the transition metals and the isocyanide was so strong, three alkali metal thiocyanates were also investigated. The isocyanide has less affinity for these cations - in complexation experiments similar to those for the transition metal salts, no complexation was observed for the thiocyanate salts of lithium, sodium or potassium.

The batch of polymer used for the h.p.l.c. work was prepared following the usual scheme (figure 1, chapter 2). The isocyanide functionalized resin was packed into stainless steel columns either

(i) under pressure at 1800 psi in the appropriate eluent or

(ii) packed dry (not under pressure).

The latter technique was used as it was felt that the 9% crosslinked resin may be too fragile to withstand packing under pressure.

Approximately 0.025 mol dm^{-3} solutions of the metal salts in aqueous tetrahydrofuran were injected into the column, and a slow flow rate (0.3 ml/min) was employed to prevent a build-up of pressure during operation (due to the fragility of the resin). An eluent of 10% tetrahydrofuran and 90% distilled water was used at first but injection of each metal solute individually gave no retention. Therefore the amount of tetrahydrofuran was increased, to provide maximum swelling of the polymer and to decrease the polarity of the eluent. The following ratios contain the maximum proportion of tetrahydrofuran whilst keeping the metal salts in solution.

60% THF/40% water for the transition metals

90% THF/10% water for the alkali metals

Again no retention was seen for any of the metal salts tested, (and therefore no separation was possible). It is therefore assumed that no weak interaction exists for the transition metals, and that the rate of complexation observed in the laboratory complexation experiments was too slow to provide a h.p.l.c. separation. In the case of the alkali metals, it is assumed that any interaction between the isocyanide group and the metal is too weak to provide a separation. These results were observed for columns packed dry and under pressure, and an investigation of the polymer material after the h.p.l.c. attempts showed no degradation of the isocyanide group. One of the problems encountered in the h.p.l.c. work is the solubility of the metal salts in the eluents used. Usually the eluent would be changed to enhance a separation - however the metal salts are insoluble in most common organic solvents and therefore the technique is limited to solvents which are miscible with water. The polymer-supported isocyanide must be present in a good swelling solvent so that the functional groups are accessible, and this solvent must be miscible with water (needed to dissolve the metal salts) and be of low polarity. Thus the choice is limited to aqueous tetrahydrofuran. However, no retention (or separation) is seen with this eluent system.

(6) Complexation from organic media

These reactions were carried out in a similar way to those using tetrahydrofuran, but under a dry nitrogen atmosphere, using dry solvents.

(a) Cobalt (II), Iron (II) and Manganese (II).

Although Sacco and Freni[44] claimed that an unstable blue form of the methyl isocyanide complex $[Co(CNMe)_5][ClO_4]_2$ was isolated from the reaction of a large excess of methyl isocyanide with cobalt(II) perchlorate in absolute ethanol, Pratt and Silverman [22] were unable to reproduce the results. These latter authors always obtained the more stable red dimeric form $[Co_2(CNMe)_{10}][ClO_4]_4$, though the presence of $[Co(CNMe)_5][ClO_4]_2$ in dilute solution at low temperatures was confirmed by the blue coloration of the solution. However, the authors describe the formation of a blue solution on dissolving the red dimeric complex $[Co_2(CNMe)_{10}][ClO_4]_4$ in water which has a similar ultraviolet spectrum to that of the blue phenyl isocyanide-cobalt complex $[Co(CNPh)_5(ClO_4)_2\ 1.5H_2O]$, and therefore concluded that the analogous, methyl isocyanide-cobalt complex is present when the red dimer is dissolved in water.

The reaction of cobalt(II) halides with isocyanide yields complexes of stoichiometry $CoX_2(CNR)_2$ and $CoX_2(CNR)_4$; (X=halogen, R=alkyl or aryl)[45]. Many members of the $CoX_2(CNR)_4$ series were found to exhibit two forms [26,44] α and β, where the α form is stable at lower temperatures and is diamagnetic.

The complex $CoCl_2(CNBu^t)_4$ is suggested as an intermediate in the cobalt-catalysed substitution of carbon monoxide by isocyanide to yield $M(CO)_{6-n}(RNC)_n$, (M=chromium, molybdenum or tungsten). This was confirmed by the addition of cobalt chloride hexahydrate to t-butyl isocyanide, in a 1:4 ratio, to yield a blue-black crystalline material thought to be $CoCl_2(CNBu^t)_4$.[46]

The analytical data for the blue-coloured polymer-supported isocyanide-cobalt complex obtained by complexation of cobalt(II) chloride from anhydrous tetrahydrofuran under a dry nitrogen atmosphere, is most consistent with the formulation of the complex as $CoCl_2(CNR)_2$. There is no evidence for reduction to cobalt(I) in the infrared spectrum (figure 19). The band due to the isocyanide stretch is at 2225 cm^{-1}, similar to those for $CoCl_2(CNCH_3)_4$,(2227 cm^{-1}) and $CoCl_2(CNCH_3)_2$,(2260 cm^{-1})[8] but in contrast to the much lower frequencies of 2195 and 2139 cm^{-1} for the reduced complex $[Co(CNCH_3)_5]ClO_4$.[23].

Arshady and co-workers[2] have reported that cobalt chloride reacted with an isocyanide-functionalized polymer support, but no further experimental details are given.

Isolated iron(II)-isocyanide complexes are commonly of the stoichiometry $Fe(CNR)_4X_2$ (X=Cl,Br,I; R=alkyl or aryl). These complexes were isolated in two forms[47], one which was intensely coloured (green or blue) and sparingly soluble, the other was brown or yellow and very soluble in organic solvents. These two forms were assumed to be cis/trans isomers. In experiments performed by Mays and Prater[48] the product was the trans-isomer, $FeCl_2(p\text{-}CH_3OC_6H_4NC)_4$, (as a blue precipitate) which was found to isomerize rapidly in chloroform solution, giving the cis-isomer (orange crystals) on addition of ether to the solution. Treatment of the complex with sodium perchlorate in acetone at room temperature gave $[FeCl(ArNC)_5][ClO_4]$ as the principal product, whereas Bonati and Minghetti isolated the latter and $[Fe(ArNC)_6][ClO_4]_2$, (Ar=p-tolyl), in their study of isocyanide complexes of iron(II)[49].

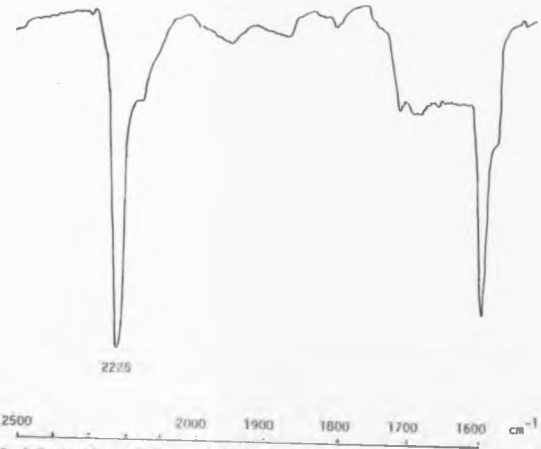


Figure 19. I.R. spectrum of the product from the reaction of $CoCl_2$ with the polymer-supported isocyanide.

In early work by Malatesta[50], the production of unstable complexes of composition $FeSO_4(CNR)_2$ and $FeCl_2(CNR)_2$ is described. These complexes, (R=alkyl or aryl), were crystalline products and were decomposed in solvent. Their structures were not investigated further and no mention of such complexes could be found in later literature.

The polymer-supported isocyanide-iron(II) complex has an infrared isocyanide band at 2190cm^{-1} (figure 20) which is in keeping with values for the isocyanide stretch of other iron(II)-isocyanide complexes:

$[Fe(p\text{-}CH_3C_6H_4NC)_6][ClO_4]_2$ 2190cm^{-1}

$[FeCl(p\text{-}CH_3C_6H_4NC)_5][ClO_4]$ 2216 (w) 2155 (br) cm^{-1}

$cis\text{-}FeCl_2(p\text{-}CH_3OC_6H_4NC)_4$ 2195, 2160, 2140 cm^{-1}

The value for the polymer-supported complex might have been expected to be up to 50 cm^{-1} higher to account for the alkyl nature of the isocyanide in the latter. However, the analytical figures are in good agreement with the assignment of the formula $FeCl_2(CNR)_2$ for the supported complex.

A recent preparation of $MnX_2(CNR)$ adducts has been described[51]. (X=Cl,Br,I;R=Bu^{t}NC) by the reaction of anhydrous manganese salts with the isocyanide in toluene. However no complexation of manganese(II) chloride from anhydrous tetrahydrofuran or ethanol solutions was observed for the polymer-supported isocyanide (figure 21).

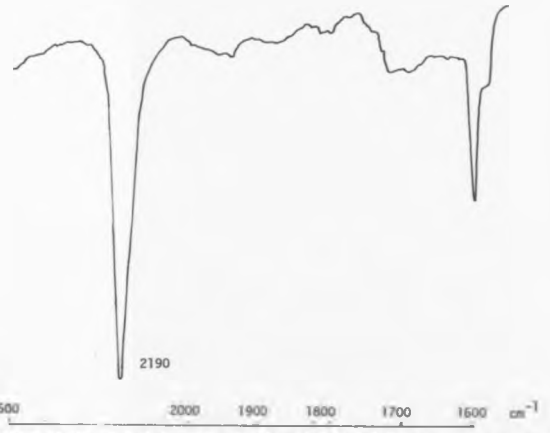


Figure 20. I.R. spectrum of the product from the reaction of $FeCl_2$ with the polymer-supported isocyanide.

Figure 21. I.R. spectrum of the product of the reaction of the polymer-supported isocyanide with $MnCl_2$.

(b) The rhodium dimers $[Rh(CO)_2Cl]_2$ and $[Rh(cod)Cl]_2$.

The dimers $[Rh(CO)_2Cl]_2$ and $[Rh(cod)Cl]_2$, where cod is 1,5-cyclooctadiene, both react rapidly with the polymer-supported isocyanide in toluene to yield supported complexes whose infrared spectra are shown in figures 22 and 23. The reaction is complete in a few hours, in contrast to 24 hours which is required for most of the metal complexation reactions in aqueous tetrahydrofuran. In the case of the $[Rh(cod)Cl]_2$ complex, gas chromatographic analysis of the supernatant liquid shows the loss of approximately one mole of 1,5-cyclooctadiene per mole of dimer. This is consistent with initial bridge cleavage (of the chlorine bridged dimer) followed by partial displacement of cod to yield a mixture of $Rh(cod)(CNR)Cl$ and $Rh(CNR)_3Cl$ on the polymer support. The reaction of the dimer with monomeric isocyanides in solution generally yields salts of the $[Rh(CNR)_4]^+$ cation[52], although the reaction may be stopped at the $[Rh(CNR)_3Cl]$ stage either by use of the appropriate deficiency of isocyanide or by use of bulky R groups in the isocyanide ligand[54]. In the case of the former, addition of the appropriate amount of 2,6-dimethylphenyl isocyanide to $[Rh(cod)Cl]_2$ allowed the isolation of $RhCl(CNR)_3$, but addition of further isocyanide yielded $[Rh(CNR)_4]Cl$. However in the case of the bulky isocyanide 2,4,6-tri-t-butylphenyl isocyanide the product was $Rh(C_{18}H_{29}NC)_3Cl$ only[54].

Addition of isocyanide to $[Rh(CO)_2Cl]_2$ has been shown to yield a variety of products. The cationic complexes $[Rh(CNR)_4]^+$ were commonly obtained [30,55], all the originally co-ordinated ligands being replaced when an excess of isocyanide was used. Deeming undertook an in situ study of the reaction of $[Rh(CO)_2Cl]_2$ with t-butyl isocyanide; the reaction was shown to yield sequentially cis-$Rh(CO)_2(CNR)Cl$, trans-$Rh(CO)(CNR)_2Cl$ and finally $[Rh(CNR)_4]Cl$.

Figure 22. I.R. spectrum of the product from the reaction of the polymer-supported isocyanide with $\left[Rh(CO)_2Cl\right]_2$.

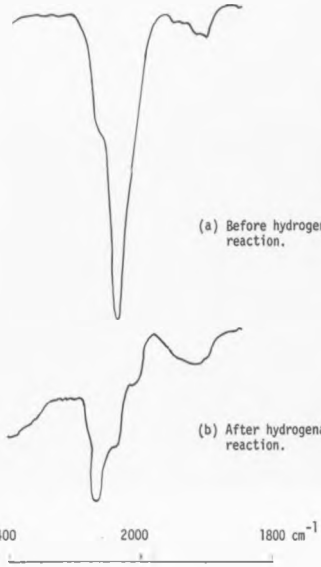


Figure 23.

I.R. spectra of the product from the reaction of the polymer-supported isocyanide with $[Rh(cod)Cl]_2$ before and after hydrogenation reaction.

A table of infrared data for these complexes is given below:

	cis-$Rh(CO)_2LCl$		trans-$Rh(CO)L_2Cl$		$[RhL_4]Cl$	
	L_1	L_2	L_1	L_2	L_1	L_2
$\bar{\nu}CO$ cm^{-1}	2101 2033	2101 2033	2009	2011	-	-
$\bar{\nu}_{NC}$ cm^{-1}	2237	2223	2197	2181	2181	2167

L_1 = $CN(CH_2)_3Si(OEt)_3$ ref 7

L_2 = Bu^tNC ref 56

The weak carbonyl band at 2100 cm^{-1} in the infrared spectrum of the polymer-supported complex (figure 24a) indicates the presence of $Rh(CO)_2(CNR)Cl$, although the more intense bands at 2008 and 2197 cm^{-1} (carbonyl and isocyanide respectively) may be assigned to $Rh(CO)(CNR)_2Cl$. The latter was confirmed by a displacement reaction with triphenylphosphine to yield a resin exhibiting only a free isocyanide stretch (2140 cm^{-1}) on the infrared spectrum, (see figure 24b) and a solid yellow product assigned as $Rh(CO)(PPh_3)_2Cl$ from the infrared spectrum, (figure 24c) which shows the carbonyl stretching band at 1975 cm^{-1} (literature value 1960 cm^{-1})[57].

Thus, both reactions of the polymer-supported isocyanide with the rhodium dimers proceed via bridge cleavage followed by partial ligand substitution, (cyclooctadiene or carbon monoxide).

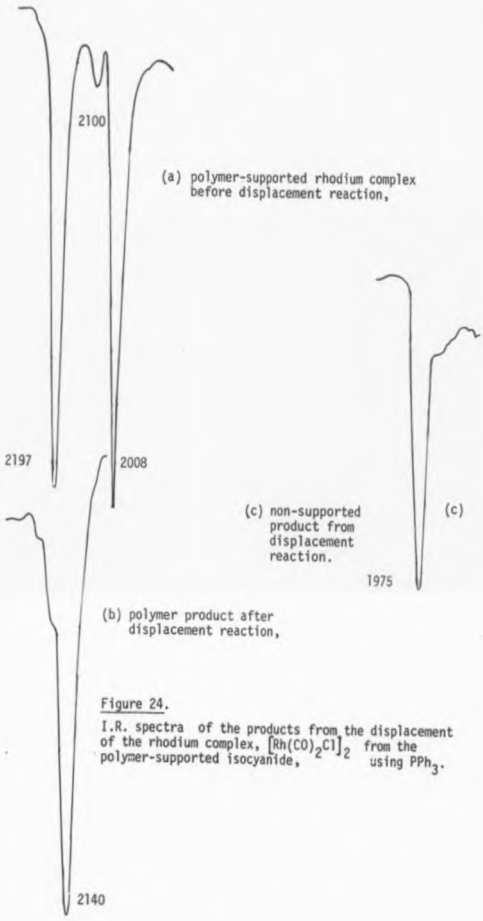


Figure 24.

I.R. spectra of the products from the displacement of the rhodium complex, $[Rh(CO)_2Cl]_2$ from the polymer-supported isocyanide, using PPh_3.

(c) Zerovalent Platinum, Palladium and Nickel

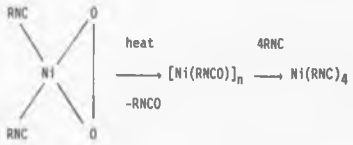
Alkyl isocyanides react with bis(1,5-cyclooctadiene)platinum to yield complexes of empirical formula $Pt(CNR)_2$, which are actually $Pt_3(CNR)_6$ trimers, (R=methyl, ethyl, t-butyl, cyclohexyl).[58] However, the analogous nickel complex reacts with an excess of alkyl or aryl isocyanide ligand to yield $Ni(CNR)_4$[59], but with a deficiency of isocyanide, the product was the nickel cluster $Ni_4(CNR)_7$. These two complexes were also the products in the reaction of $(cod)_2Ni$ with bulky isocyanides, such as t-butyl or isopropyl isocyanide[60], in the ratios indicated:

$$(cod)_2Ni + xRNC \longrightarrow 2\ cod + [(4-x)/9]Ni_4(CNR)_7 + [(4x-7)/9]Ni(CNR)_4$$

Vacuum thermolysis of $Ni_4(CNBu^t)_7$ at 60 °C leads to the loss of isocyanide to yield $Ni_4(CNBu^t)_6$, which has also been obtained by the direct reaction of $(cod)_2Ni$ and the appropriate amount of isocyanide. Red-black insoluble solids with metal to isocyanide ratios of between 1:1 and 1:1.25 were also produced in the reaction of non-bulky isocyanides (i.e. R=CH_3, C_2H_5, Bu^n, CH_2Ph) with $(cod)_2Ni$. All these nickel-isocyanide complexes exhibit terminal and bridging (~1600-1700 cm^{-1}) isocyanide stretching frequencies in their infrared spectra; examples are given below:

Complex	Terminal $\bar{\nu}_{NC}$ cm^{-1}	Bridging $\bar{\nu}_{NC}$ cm^{-1}
$Ni_4(CNC_6H_{11})_7$	2075 (vs)	1700 (s) 1600 (s)
$Ni_4(CNCH(CH_3)_2)_6$	2095 (s) 2050	1715-1750 (m)

The nickel isocyanide complexes are extremely air sensitive; the complexes $Ni(CNBu^t)_4$ and $Ni_4(CNR)_7$ react with oxygen to give $NiO_2(CNR)_2$ adducts[61]. When the complex $NiO_2(CNBu^t)_2$ was suspended in toluene and stirred at ambient temperature, oxygen transfer to the isocyanide ligand occured to yield one mole of t-BuNCO and a brown complex (assumed to be $[Ni(RNCO)]_n$ polymer). By treating the latter complex with excess tertiary butyl isocyanide, $Ni(CNBu^t)_4$ was regenerated.



Reaction of $(cod)_2Ni$ and $(cod)_2Pt$ with the polymer-supported isocyanide yields supported complexes of stoichiometry M(CNR) and is accompanied by quantitative displacement of cyclooctadiene (confirmed by gas chromatography). The supported platinum complex exhibits a well-defined isocyanide band at 2150 cm^{-1} in its infrared spectrum (figure 25); however the analogous nickel complex shows only a very broad band centred at 2205 cm^{-1} and a weak absorption at 2140 cm^{-1} due to free isocyanide (figure 26). Due to unavoidable oxidation during preparation for spectroscopy, the infrared is most consistent with Ni(RNCO) as the supported species; long exposure to air results in a colour change from red-brown to yellow-green.

There would appear to be no reported analogue of the supported Pt(CNR) species; the broad absorption seen at approximately 1715 cm^{-1} in

Figure 25. I.R. spectrum of the product from the reaction of the polymer-supported isocyanide with $Pt(cod)_2$.

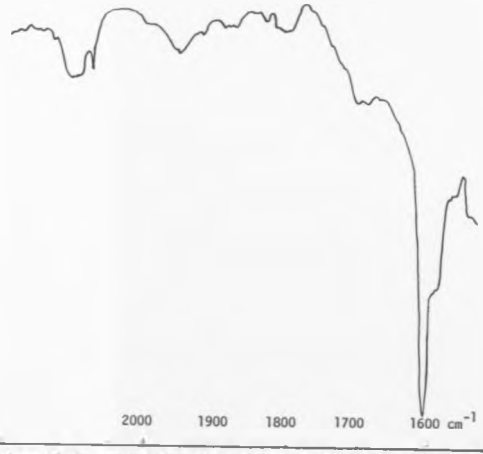


Figure 26. I.R. spectrum of the product from the reaction of the polymer-supported isocyanide with $Ni(cod)_2$.

the infrared spectrum (figure 25) may be slightly more pronounced than that found in the uncomplexed isocyanide (present due to polymerization of the isocyanide during its preparation) and so may obscure the presence of any bridging isocyanide vibration, or it may be that co-ordinated solvent (toluene) is present to maintain co-ordinative saturation.

Complexes of stoichiometry $Pd(CNR)_2$ have been prepared by either the reaction of a solution of $(dba)_3Pd_2.(CHCl_3)$ and methyl isocyanide in acetonitrile with $[(CH_3NC)_4Pd][PF_6]_2$ or alternatively the addition of solid $(dba)_3Pd_2.(CHCl_3)$ to a stirred solution containing $[(CH_3NC)_4Pd]^{2+}$ and an excess of free methyl isocyanide[19] (dba=dibenzylidene acetone). A trimeric structure is suggested. Addition of excess methyl isocyanide to solutions of $(dba)_3Pd_2.(CHCl_3)$ in acetonitrile, acetone or dichloromethane produced a yellow solution which was stable in the absence of air, and although the exact composition of the species was not determined (described as $(CH_3NC)_xPd$), addition of iodine yielded $(CH_3NC)_2PdI_2$. Evaporation of the yellow solution produced a dark brown solid with an isocyanide band at 2185 cm^{-1} in its infrared spectrum. The palladium complex prepared by the reaction of $(cod)_2Pd$ and two equivalents of t-butyl isocyanide having the composition $Pd(CNBu^t)_2$ was determined to be the trimeric species $Pd_3(CNBu^t)_6$[62].

The product of the reaction of the polymer supported isocyanide with $Pd(dba)_2$ has a stoichiometry of $Pd(CNR)_2$ from the analytical data, although the infrared spectrum (figure 27) is more difficult to interpret. There is a broad absorption around 2197 cm^{-1} (with a slight shoulder at 2267 cm^{-1}) due to the complexed isocyanide, which is similar to that of the dark brown solid described earlier, 2185 cm^{-1}. There is also some evidence of bridging isocyanide absorption at around 1720 cm^{-1}, although the presence of polymerized isocyanide in the spectrum of uncomplexed isocyanide also has a weak, broad absorption in this region.

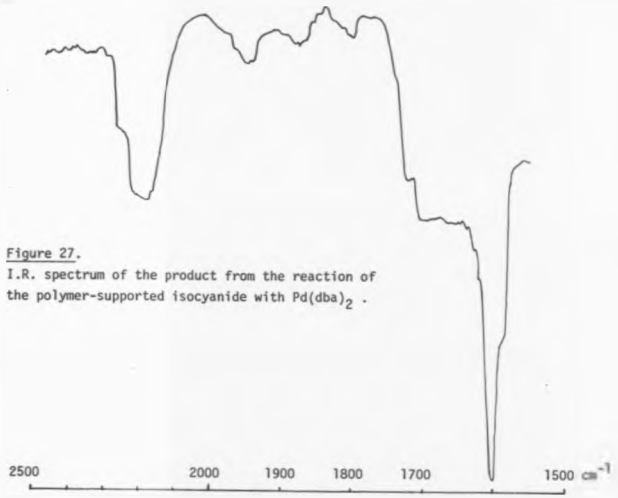


Figure 27.
I.R. spectrum of the product from the reaction of the polymer-supported isocyanide with $Pd(dba)_2$.

(7.) Catalysis

The supported rhodium(I) complexes prepared by reaction of the dimers $[Rh(CO)_2Cl)_2$ and $[Rh(cod)Cl]_2$ with the polymer-supported isocyanide were investigated as potential catalysts for the hydrogenation of cyclohexene. Under the conditions used,(1 atm H_2,60 ^oC) only the latter complex was found to be active. Although the reaction appears to proceed with no loss of metal (rhodium analyses before and after hydrogenation were identical) the following observations indicate that some or all of the catalysis proceeds via reduction to the metal. An induction period of about 100 minutes is observed, after which catalysis activity increases with time (see figure 28); similar results were found for rhodium catalysts anchored on silica supports[7,63] where induction periods were observed, and reduction to metal is assumed. Metal crystallite formation or reduction of the metal complex has been observed for both a polymer-supported $[Rh(CO)_2Cl]_2$ catalyst anchored via a cyclopentadienyl group on a 20% crosslinked polystyrene resin[64], and for a similar rhodium complex anchored on both 8% crosslinked polystyrene and soluble polystyrene supports[65].

In the case of our polymer-supported rhodium complex, there is also a large decrease in the intensity of the infrared CN vibration at 2165 cm^{-1} (figure 23), together with the appearance of a band at 2230 cm^{-1}. These changes are similar to those observed on hydrogenation using a silica-supported catalyst[7] and may be due to the hydrogenation of the isocyanide coupled perhaps with metal catalysed isomerisation to the nitrile (expected CN vibration ~ 2250-2300 cm^{-1}).

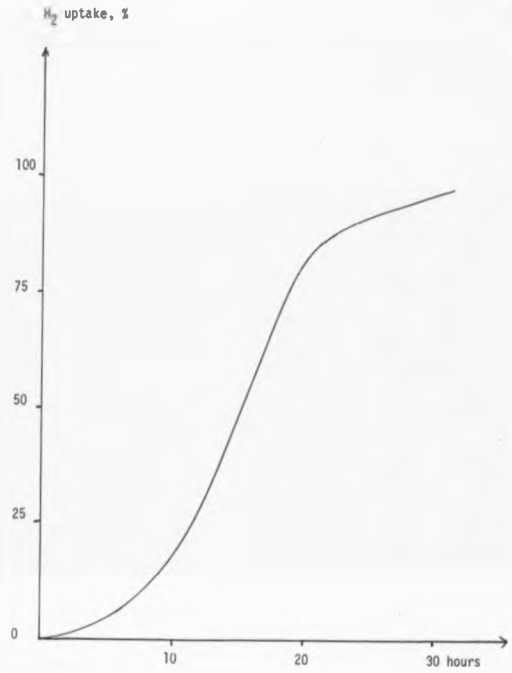
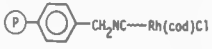


Figure 28.

Graph to show the rate of hydrogenation of cyclohexene to cyclohexane catalysed by



3.3 EXPERIMENTAL

(A)Metal Complexation

(1.1) Complexation from aqueous tetrahydrofuran.

Polymer-supported isocyanide (0.2 g, 0.21 mmol isocyanide) was swollen in tetrahydrofuran (5 ml); and tetrachloroauric acid (0.08 g, 2.03 mmol) dissolved in distilled water (5 ml) was added to the polymer, and the mixture was stirred overnight. The polymer was filtered, washed with water, ethanol, diethyl ether and then dichloromethane, and dried under vacuum for 24 hours.

This procedure was followed for all other metal salts complexed from aqueous tetrahydrofuran i.e. K_2PtCl_4, Na_2PdCl_4, $RhCl_3.xH_2O$, $AgPF_6$, $AgNO_3$, $CuCl_2.2H_2O$, $HgCl_2$ and for attempted complexation of $ZnCl_2$, $NiCl_2.6H_2O$.

The above procedure was also carried out for the following : LiSCN KSCN, NaSCN (with reference to h.p.l.c. work, section 5) but showed no complexation (i.e. no visible change in free NC stretch at 2140 cm^{-1} on the infrared spectra and no appearance of a complexed NC stretch).

1.2 Complexation from organic media.

Using a drybag, a similar procedure was followed for the complexation of anhydrous cobalt chloride and ferrous chloride from dry tetrahydrofuran only (10 ml), under a nitrogen atmosphere. The polymer product was washed with dry tetrahydrofuran and dry dichloromethane before drying under vacuum for 24 hours.

The organometallic complexes were reacted with the polymer-suported isocyanide also in the drybag, in the same way, in either dry tetrahydrofuran (for $Pd(dba)_2$) or dry toluene (for $Pt(cod)_2$, $Ni(cod)_2$, $[Rh(CO)_2Cl]_2$, and $[Rh(cod)Cl]_2$). At least 10 ml of solvent was used per 0.2 g polymer, but the amount was increased as necessary due to the relative solubilities of the metal complexes.

The polymer product in each case was washed with either dry tetrahydrofuran, or dry toluene, followed by dry dichloromethane, before drying under vacuum for 24 hours.

For a table of analysis results and infrared spectra see discussion - examples of calculations can be found at the end of the experimental section.

Table 3 Raw Analytical Data

metal complex	product colour[a]	%metal	%Cl or P	isocyanide content of polymer
$RhCl_3.xH_2O$	pale orange	2.8	3.5	0.56
K_2PtCl_4	light brown	7.9	2.8	0.90
$NaPdCl_4$	red brown	10.1	5.1	1.03
$AgNO_3$	off-white	6.4	-	1.03
$AgPF_6$	off-white	4.4	1.1	0.90
$HAuCl_4.3H_2O$	off-white	9.7	3.2	0.90
$CuCl_22.H_2O$	off-white	1.9	1.9	1.03
$HgCl_2$	pale yellow	11.5	4.0	1.03
$CoCl_2$	turquoise	2.8	3.8	1.03
$FeCl_2$	pale yellow	2.8	4.4	1.03
$Pd(dba)_2$	dark brown	5.7	-	1.03
$Pt(cod)_2$	orange-brown	13.9	-	1.03
$[Rh(cod)_2Cl]_2$	pale orange	5.8	2.5	1.03
$Ni(cod)_2$	red brown[b]	6.3	-	1.03
$[Rh(CO)_2Cl]_2$	brown	7.0	3.05	1.03

(a) colour of original polymer is light yellow brown.

(b) turns to yellow-green on prolonged exposure to air.

1.3 Metal complexation for rate determinations.

The procedure described in section (i) was followed for samples of (a) K_2PtCl_4

(b) $AgPF_6$ and Na_2PdCl_4

(c) $AgPF_6$ and K_2PtCl_4

(d) $HAuCl_4.3H_2O$ and K_2PtCl_4.

The polymer:metal mixtures were set up in separate flasks, but ran concurrently for the pairs listed. The complexation rate was determined for samples of both 2% and 9% crosslinked resins for each set (a)-(c) and 9% only for (d), by removal of small samples at approximately 1-2 hour intervals, washing as described in section 1.1, and drying under vacuum for 2-3 hours before running the infrared spectra. Approximately equimolar ratios of polymer:metal salt were used for these determinations.

Tables 4-7 Comparison of the rate of complexation of metal salts, by polymer supported isocyanides:

(i) 2% crosslinked (sample JC218)

(ii) 9% crosslinked (sample JC211)

Calculations assume the infrared bands correspond to triangles, (by counting scaled paper squares on the original spectra). i.e. base x height /2 = area.

$$\% \text{ conversion} = \frac{\text{area complexed band}}{\text{area complexed band + area free band}} \times 100$$

Table 4 K_2PtCl_4 only, with (i) and (ii)

polymer	hours	complexed ν_{NC} (area of band)	free ν_{NC} (area of band)	%conversion
(i)	1.0	7.5	60.0	11.1
(ii)	1.0	11.5	70.6	14.0
(i)	2.0	12.0	53.8	18.2
(ii)	2.0	66.4	68.1	49.4
(i)	3.0	41.0	23.0	64.1
(ii)	3.0	21.0	47.3	30.7
(i)	3.75	17.5	26.0	40.2
(ii)	3.75	51.0	21.5	70.3
(i)	5.25	33.3	19.7	62.8
(ii)	5.25	55.0	15.8	77.7
(i)	6.25	40.0	12.8	75.8
(ii)	6.25	30.0	4.1	88.0
(i)	8.5	61.9	7.0	89.8
(ii)	8.5	62.0	5.6	91.7

See graph, figure 12.

Table 5 $AgPF_6$ and Na_2PdCl_4 with polymers (i) and (ii).

polymer/metal salt	hours	complexed ν_{NC} (area of band)	free ν_{NC} (area of band)	%conversion
(i)Ag	1	38.3	10.0	79.3
(ii)Ag	1	11.0	20.0	35.5
(i)Pd	1	26.0	28.0	48.1
(ii)Pd	1	33.8	35.0	49.1
(i)Ag	3	49.5	5.1	90.7
(ii)Ag	3	73.8	45.0	62.1
(i)Pd	3	49.4	29.3	62.8
(ii)Pd	3	18.5	11.6	61.8
(i)Ag	5.25	78.8	4.1	95.1
(ii)Ag	5.25	33.8	7.1	82.6
(i)Pd	5.25	22.0	7.9	73.6
(ii)Pd	5.25	45.0	16.0	73.8
(i)Ag	7	57.8	0.75	98.6
(ii)Ag	7	35.0	6.8	83.7
(i)Pd	7	48.8	12.7	79.3
(ii)Pd	7	33.8	35.0	49.1
(i)Ag	24	58.8	0.9	98.5
(ii)Ag	24	40.0	1.9	95.5
(i)Pd	24	53.8	8.3	86.6
(ii)Pd	24	84.8	14.5	85.4

See graph, figure 13.

Table 6 $AgPF_6$ and K_2PtCl_4 with polymers (i) and (ii)

polymer/metal salt	hours	complexed ν_{NC} (area of band)	free ν_{NC} (area of band)	%conversion
(i)Ag	1	43.9	15.8	73.5
(ii)Ag	1	7.5	27.0	21.7
(i)Pt	1	11.3	51.3	18.1
(ii)Pt	1	5.0	27.5	15.4
(i)Ag	2	47.5	9.0	84.1
(ii)Ag	2	14.0	14.9	48.4
(i)Pt	2	14.1	25.0	36.1
(ii)Pt	2	12.0	23.0	34.3
(i)Ag	4	29.8	3.0	90.9
(ii)Ag	4	12.0	11.0	52.2
(i)Pt	4	12.3	19.0	39.3
(ii)Pt	4	37.1	22.5	62.2
(i)Ag	6	45.0	2.6	94.5
(ii)Ag	6	28.0	18.0	60.9
(i)Pt	6	34.0	10.5	76.4
(ii)Pt	6	60.8	21.0	74.3
(i)Ag	23	65.3	1.9	97.2
(ii)Ag	23	48.0	4.4	91.6
(i)Pt	23	141.4	4.2	97.1
(ii)Pt	23	138.0	3.8	97.3

See graph, figure 14.

Table 7 $HAuCl_4.3H_2O$ and K_2PtCl_4, with polymer (ii) only.

polymer/metal salt	hours	complexed ν_{NC}	free ν_{NC}	% conversion
(ii)Au	1	135.0	3.4	96.8
(ii)Pt	1	3.8	46.9	7.5
(ii)Au	3	136.5	0.5	99.6
(ii)Pt	3	7.5	20.5	26.8
(ii)Au	5	187.5	0.5	99.8
(ii)Pt	5	10.5	23.0	31.3

See graph, figure 15.

(1.4)Selective complexation of platinum/rhodium mixture.

The solubility of the two salts together in aqueous tetrahydrofuran was first determined by disolving K_2PtCl_4 (0.01 g) and $RhCl_3.xH_2O$ (0.06 g) in water (5 ml), followed by the addition of tetrahydrofuran (5 ml). No precipitation or reaction was observed.

K_2PtCl_4 (0.0104 g, 0.0025 mol) and $RhCl_3.xH_2O$ (0.0062 g, 0.024 mmol) were dissolved in distilled water (5 ml). This mixture was added to a reaction flask containing polymer-supported isocyanide (0.0891 g, 0.05 mmol) in tetrahydrofuran (5 ml). The reaction mixture was stirred for 24 hours. The polymer product was filtered, washed and dried as in section (i).

Analytical Data

Pt content: 2.8% 96.2 mole % of total metal incorporation

Rh content: 0.06% 3.8 mole % of total metal incorporation

I.R. spectrum (KBr disc) figure 29

Complexed NC stretch 2222 cm^{-1}

Free NC stretch 2140 cm^{-1}

(B) Attempted removal/displacement of metal complexes.

The following combinations of polymer-supported metal/solvent were tested;

(i)polymer-supported rhodium (from $RhCl_3.xH_2O$ complexation) with

(a) Dimethylformamide

(b) Dimethylsulphoxide - standard technique plus ultrasonic.

(ii)polymer-supported platinum (from K_2PtCl_4 complexation) with

(a) Dimethylsulphoxide

(b) Pyridine

(c) Piperidine -standard technique plus ultrasonic.

The following procedure is typical:

(i)(a) (standard technique)

Polymer-supported rhodium complex (0.1 g,~3 mg Rh, 0.03 mmol) was suspended in dimethylsulphoxide (5 ml) and stirred for 24 hours. The polymer product was filtered, (the filtrate was retained) and washed with water, ethanol, diethyl ether and then dichloromethane, before drying under vacuum for 4 hours. Infrared spectra of starting material and product were recorded. In some cases (as indicated above) the flask containing the reactants was suspended in an ultrasonic bath for 24 hours, instead of stirred.

Infrared spectrum (figure 30a) shows little difference between starting material and product. No evidence of free (i.e. uncomplexed) isocyanide, ($\bar{\nu}_{NC}$ 2140 cm^{-1} free)
($\bar{\nu}_{NC}$ 2214 cm^{-1} Rh complexed NC).

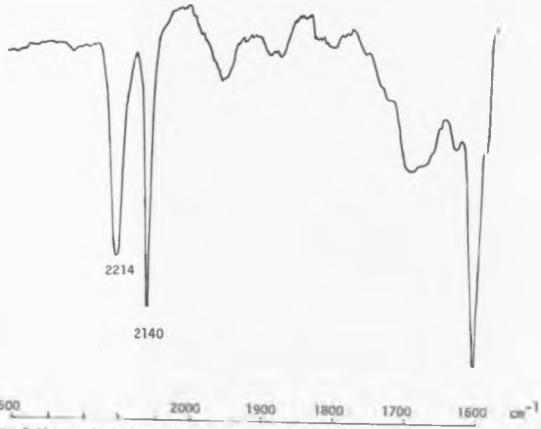


Figure 29. I.R. spectrum of the product from the reaction of the polymer-supported isocyanide with K_2PtCl_4 & $RhCl_3.xH_2O$

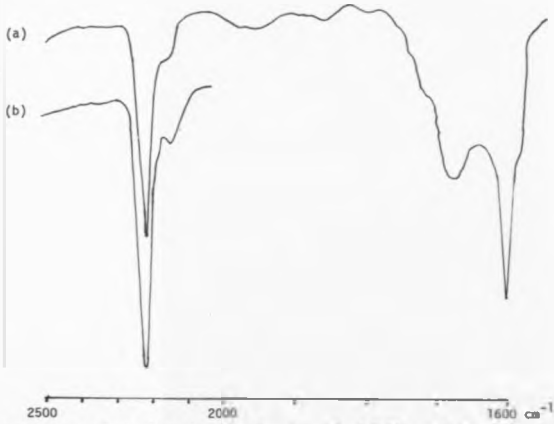


Figure 30. I.R. spectra of the products from the attempted removal of $RhCl_3.xH_2O$ from the polymer support using DMSO (a) standard technique or (b) ultrasonic technique.

For (j)(b) ultrasonic technique

0.0789 g polymer-supported rhodium complex used in 5 ml dimethylsulphoxide. (~3 mg Rh from metal analysis of starting material) standard soln: 3.2 mg $RhCl_3.xH_2O$ made up to 5 ml in DMSO

(figure 31) ultraviolet spectrum and data.

Filtrate from reaction : absorbance 0.071 at 417 nm.

Standard soln : absorbance 0.692 at 417 nm.

Therefore approximately 1/10 of rhodium removed.

Infrared spectra (figure 30b) shows very slight shoulder at 2140 cm^{-1}

Polymer-supported metal	solvent	technique	infrared spectrum before/after comments
Rh	DMF	stir	no change(no free ν_{NC})
Rh	DMSO	stir	no change(no free ν_{NC})
Rh	DMSO	ultrasonic	very slight shoulder at 2140 cm^{-1}-free ν_{NC}
Pt	DMSO	stir	no change
Pt	Pyridine	stir	no change
Pt	Piperidine	stir	shoulder at 2140 cm^{-1} -free ν_{NC}
Pt	Piperidine	ultrasonic	disappearance of complexed ν_{NC} at 2222 cm^{-1}, no free ν_{NC} at 2140 cm^{-1}

(iii) polymer-supported silver. with triphenylphosphine.

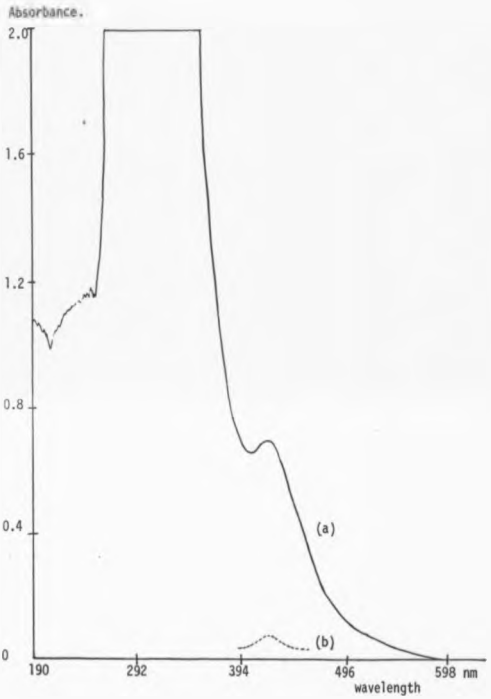
Polymer-supported silver complex (from complexation with $AgPF_6$)(0.11 g, max 0.09 mmol Ag) was swollen in dichloromethane (15 ml) and triphenylphosphine (0.05 g, 0.2 mmol) was added. The mixture was

Figure 31.

Attempted removal of $RhCl_3.xH_2O$ from the polymer-supported isocyanide using DMSO, (ultrasonic technique).

(a) Std $RhCl_3.xH_2O$ soln. in DMSO, abs: 0.692 at 417nm.

(b) Soln from attempted extraction of rhodium salt, abs: 0.071 at 417nm.



stirred and refluxed for 3 days. The polymer product was filtered, washed with dichloromethane, and dried under vacuum for 6 hours. The infrared spectrum (figure 17) shows the presence of a considerable proportion of free isocyanide, estimated (as for the rate determinations) to be approximately 60% free, 40% complexed isocyanide.

(C) Attempted h.p.l.c. separations of metal salts

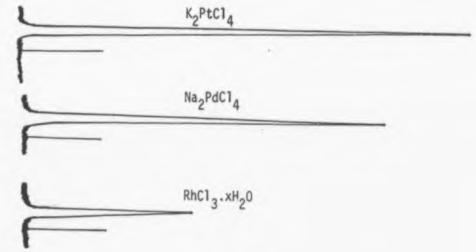
This work was carried out, by the author, at Polymer Laboratories, using Knauer h.p.l.c. equipment, with a conductivity detector. Standard stainless steel columns were used, all with internal diameter 4.6 mm. Columns were packed dry or at 1800 psi in the eluent shown. Columns were packed with the polymer-supported isocyanide, (JC211), 9% crosslinked, 0.9 mmol g^{-1}.

Table 8 Conditions used.

figure no.	flow Rate (ml/min)	how packed	length of column (cm)	eluent % THF (rest H_2O)	to separate
32	0.3	1800 psi/ 10%THF	15	10	transition metal cations and alkali
33	0.3	dry	5	10	metal cations
34	0.3	dry	15	60	transition metal cations
35	0.3	dry	15	90	alkali metal cations
35	0.3+ 1.0	1800 psi/ 60%THF	15	60	transition metal cations

Chart speed 300 mm/hr

Approximately 0.025 mol dm^{-3} solutions of the following metal salts were prepared by accurately weighing the approprate amount of metal salt and dissolving in the appropriate eluent. The injection volumes were in the range 2.5-10 ul. It can be seen from the h.p.l.c. traces



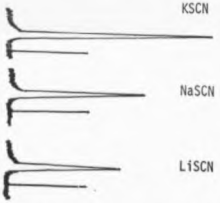


Figure 32. H.p.l.c. traces of attemped separation using the polymer-supported isocyanide.

Column packed dry, eluent: 10% THF in H_2O, metal salts 0.025M.

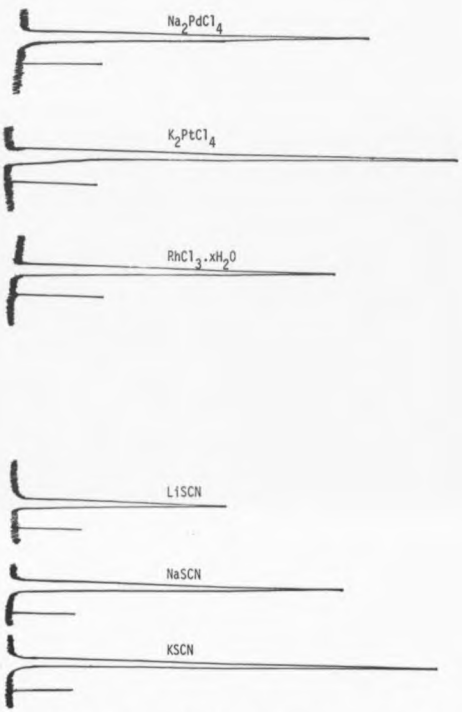


Figure 33. H.p.l.c. traces of attempted separartion using the polymer-supported isocyanide.

Column packed at 1800psi in eluent, eluent: 10% THF in H_2O, metal salts 0.025M.

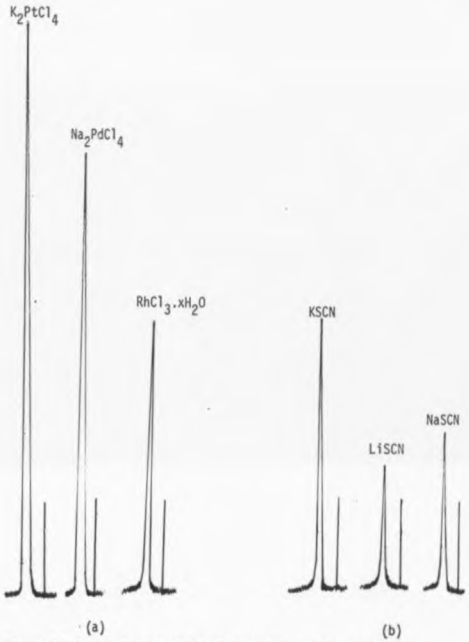


Figure 34. H.p.l.c. traces of attempted separation using the polymer-supported isocyanide.

Column packed dry, eluent: (a) 60% THF in H_2O, (b) 90% THF in H_2O, metal salts 0.025M.

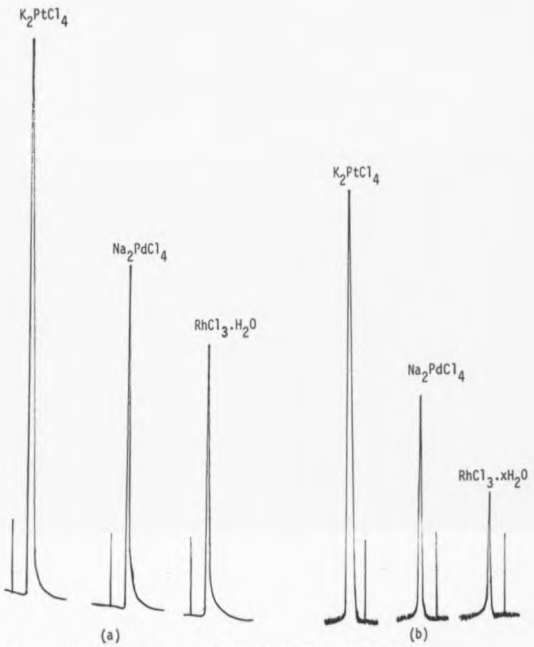


Figure 35. H.p.l.c. traces of attempted separation using the polymer-supported isocyanide.

Column packed at 1800psi in eluent, eluent: 60% THF in H_2O, metal salts 0.025M.

Flow rates: (a) 1.0 ml/min, (b) 0.3 ml/min.

(figures 32-35) that all the metal solutions (injected singly) showed no retention and were washed straight through the column under all conditions used. Therefore no separation would be possible.

Samples used: K_2PtCl_4
$RhCl_3.xH_2O$
Na_2PdCl_4
LiSCN
NaSCN
KSCN

Polymer stability

The I.R. spectrum of the isocyanide-functionalized resin showed a sharp NC stretch at 2140 cm^{-1}, before and after the h.p.l.c. work.
NC titration before: 0.90 mmol g^{-1}
after: 0.87 mmol g^{-1}

(D) Organometallic complexes, preparation, reaction and analysis of products

$[Rh(CO)_2Cl]_2$[66], $[Rh(cod)Cl]_2$[67], $Ni(cod)_2$[68]
$Pt(cod)_2$[69], $Pd(dba)_2$[70] were prepared by the literature methods, and complexed by the isocyanide as described in section A,(ii)

Determination of cod loss in metal complexation by the polymer supported isocyanide

$Ni(cod)_2$, $Pt(cod)_2$ and $[Rh(cod)Cl]_2$ were also reacted with an

excess of isocyanide (rather than an excess of metal) in a similar manner to that of section (A)(ii). Approximately 0.5 g of polymer-supported isocyanide were used, in 10 ml dry toluene, with an appropriate amount of complex.

Two standard solutions of cod in toluene were also prepared, corresponding to the loss of one or both cod's from the metal complexes, for use in gas chromatographic determination.

sample	sample		poly MC		toluene	
	wt(g)	mmol	wt(g)	mmol	ml	
$Pt(cod)_2$	0.0969	0.24	0.5175	0.53	10	
$Ni(cod)_2$	0.0742	0.27	0.5172	0.53	10	
cod	0.572	0.53	-	-	10	std A
cod	0.0235	0.22	-	-	10	std B
$[Rh(cod)Cl]_2$	0.0531	0.108	0.3221	0.33	10	

After filtration of the polymer product, a sample of the filtrate (for each of the reactions and standards) was analysed by gas chromatography.

Conditions used:

Column: SE30, 5% on chromosorb W, 19 ft.

temp: 135 ^{o}C

samples: 1µl

attenuation: $1x10^4$

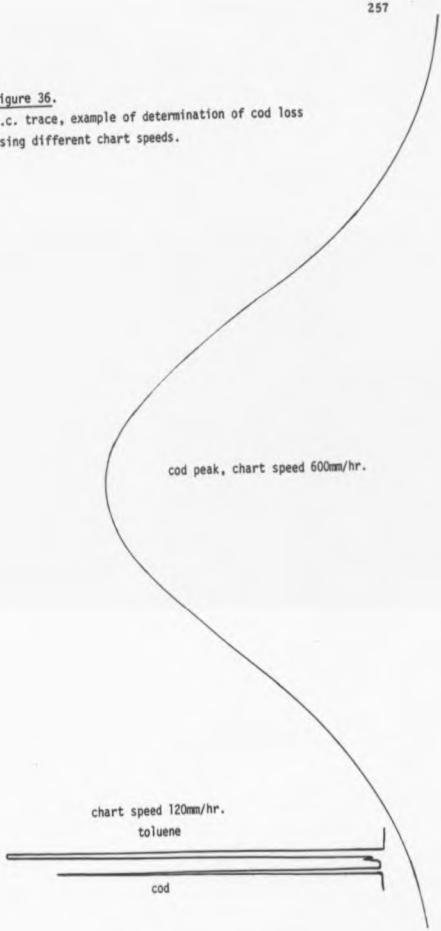
N_2 flow rate : 30 ml/min.

Chart speed: 120 mm/hr.

For cod determinations: figure 36 shows a typical trace.

Chart speed: 600 mm/hr

Figure 36.
G.c. trace, example of determination of cod loss using different chart speeds.



Peaks cut out and weighed:-

weights of peaks:

standard A;	0.6172 g	~2 cod
standard B;	0.2337 g	~1 cod
$Pt(cod)_2$/poly NC;	0.4590 g	~2 cod
$Ni(cod)_2$/poly NC;	0.6163 g	~2 cod
$[Rh(cod)Cl]_2$/poly NC;	0.1303 g	~1 cod

(ii) Reaction of polymer-supported isocyanide-rhodium carbonyl complex with triphenylphosphine.

Polymer-supported isocyanide-rhodium carbonyl complex (0.4815 g, ~0.29 mmol Rh) was swollen in toluene (35 ml, dried and distilled off sodium wire) for 30 minutes. Triphenylphosphine (0.1721 g, 0.66 mmol) was added and the mixture stirred for 6 hours at room temperature. The polymer product was filtered, washed with dry toluene and dried under vacuum. The solvent was removed from the filtrate to yield a yellow solid which was also dried under vacuum.

I.R.(KBr discs) (figure 24 in discussion).

(a) poly-NC:$[Rh(CO)Cl]_2$ complex before reaction

ν_{CO} 2008(s), 2100(w) cm^{-1}; ν_{CN} 2197(s) cm^{-1}

(b) polymer as in (a), after reaction

ν_{CN} 2140 cm^{-1}

(c) yellow solid product from reaction

ν_{CO} 1980 cm^{-1}

(E) Catalysis

Hydrogenation of cyclohexene to cyclohexane.

Polymer-supported $[Rh(CO)_2Cl]_2$ and $[Rh(cod)Cl]_2$ were tested in the following way; however only the latter acted as a catalyst for the reaction.

The polymer-supported $[Rh(cod)Cl]_2$ complex (0.12 g 2.4% Rh) was swollen in toluene (2 ml, dry, distilled off sodium wire) for 5 minutes, and cyclohexene (1 ml of 7.3 M solution in toluene) was added. The solution was rapidly stirred under 1 atm hydrogen at 60 °C until hydrogen uptake had ceased.

Complete conversion was confirmed by gas chromatography, under the following conditions:

column: SE30, 5% on chromosorb W 19 ft

temp: 50 °C

sample: 0.5µl

chart speed : 120 mm/hr

N_2 flow rate: 30 ml/min

No conversion was observed for the supported complex $[Rh(CO)_2Cl]_2$.

100% conversion was observed for the supported complex $[Rh(cod)Cl]_2$.

Rh analysis of supported complex after hydrogenation = 2.4%.

I.R. (KBr discs) of supported complex $[Rh(cod)Cl]_2$

Before catalysis: (figure 23a)

	cm^{-1}
ν_{CN}:	2130(sh)
	2165(s)
	2215(sh)

After catalysis: (figure 23b)

	cm^{-1}
ν_{CN}:	2165(w)
	2230

(F) Calculations

Examples of method of calculation for comparison with analytical values for metal and chlorine or phosphorus content of polymer.

The calculations are all based on the reaction equations shown in table 2. Most follow the same pattern of reaction of the isocyanide with the metal with no reduction of the metal. An example is given overleaf:

(a)For platinum:

Proposed reaction:

$$K_2PtCl_4 + 2RNC \longrightarrow PtCl_2(RNC)_2 + 2KCl.$$

Isocyanide content of polymer = 0.9 mmol g^{-1}

wt gain by polymer : (0.5)(0.9)(415.08) = 186.78 mg

wt loss by polymer : (0.9)(74.55) = 67.10 mg

net wt gain = 119.69 mg for 1 g of polymer.

$$\therefore \text{Amt Pt present} = \frac{(0.5)(0.9)}{1.1197} = 0.40 \text{ mmol } g^{-1}$$

$$\therefore \text{Amt Cl present} = \frac{(1)\ (0.9)}{1.1197} = 0.80 \text{ mmol } g^{-1}$$

Similar calculations were carried out for the following metals salts:

Na_2PdCl_4, $RhCl_3.xH_2O$, $AgNO_3$, $AgPF_6$, $FeCl_2$, $CoCl_2$,
$Pd(dba)_2$, $[Rh(cod)Cl]_2$, $Pt(cod)_2$ and $[Rh(CO)_2Cl]_2$.
(Note : for rhodium salt, calculations assumes x=3).
For those metals which underwent reduction as well as complexation, the following calculations were made:

(b) For copper

Proposed reaction:

$$2CuCl_2 + 5RNC + 2H_2O \rightarrow 2CuCl(CNR)_2 + HCl + CO_2 + RNH_3Cl.$$

Isocyanide content of polymer = 1.03 mmol g^{-1}

wt gain by polymer : (0.4)(1.03)(134.5) + (0.4)(1.03)(18)

= 62.83 mg

wt loss by polymer : (0.2)(1.03)(36.5) + (0.2)(1.03)(44)

= 16.58 mg

net wt gain = 46.25 mg for 1 g of polymer.

$$\therefore \text{Amt Cu present} = \frac{(0.4)(1.03)}{1.0463} = 0.39 \text{ mmol } g^{-1}$$

$$\therefore \text{Amt Cl Present} = \frac{(0.4)(1.03) + (0.2)(1.03)}{1.0463}$$

= 0.59 mmol g^{-1}

(c) For gold:

Proposed reaction:

$HAuCl_4 + 2H_2O + 2RNC \rightarrow AuCl(CNR) + CO_2 + 2HCl + RNH_3Cl$

Isocyanide content of polymer = 1.03 mmol g^{-1}

wt gain by polymer : (0.5)(1.03)(340) + (1)(18)

= 193 mg

wt loss by polymer : (0.5)(1.03)(44) + (1)(36.5)

= 59.1 mg

net wt gain = 133.9 mg for 1 g of polymer

$\therefore$ Amt Au present $= \frac{(0.5)(1.03)}{1.1339} = 0.45$ mmol g^{-1}

$\therefore$ Amt Cl present $= \frac{(1)(1.3)}{1.1339} = 0.90$ mmol g^{-1}

(d) For mercury:

Proposed overall reaction (1)

$HgCl_2 + 1.7\ CNR \rightarrow 0.7\ HgCl_2(CNR)_2 + 0.3\ HgCl_2(CNR)$

Isocyanide content of polymer = 1.03 mmol g^{-1}

For reaction $HgCl_2 + 2\ CNR \rightarrow HgCl_2(CNR)_2$

wt gain by polymer : (0.5)(1.03)(271.5) = 139.8 mg

(no wt loss)

$\therefore$ Amt Hg present $= \frac{(0.5)(1.03)}{1.1398}$ = 0.45 mmol g^{-1}

$\therefore$ Amt Cl present $= \frac{(1.03)}{1.1398}$ = 0.90 mmol g^{-1}

For reaction $HgCl_2 + CNR \rightarrow HgCl_2(CNR)$

wt gain by polymer : (1.03)(271.5) = 279.6 mmol g^{-1}

(not wt loss)

$\therefore$ Amt Hg present $= \frac{1.03}{1.2796}$ = 0.80 mmol g^{-1}

$\therefore$ Amt Cl present $= \frac{(1.03)(2)}{1.2976}$ = 1.60 mmol g^{-1}

From Cl Figures:

$x(0.90) + (1-x)(1.60) = 1.12$

$0.90\ x + 1.60 - 1.60x = 1.12$

$-0.7x = -0.48$

$\therefore \quad x = 0.69.$

Overall calculations:

for 0.7 $HgCl_2(CNR)_2$ + 0.3 $HgCl_2(CNR)$

$\therefore$ Amt Hg present = (0.7)(0.45) + (0.3)(0.80)

= 0.56 mmol g^{-1}

$\therefore$ Amt Cl present = 1.12 mmol g^{-1}

Proposed reaction (ii)

Of 1.03 mmol g^{-1} isocyanide present, assume only 0.66 mmol g^{-1} is available for complexation, the rest having been polymerized.

Proposed reaction:

$HgCl_2$ + CNR $\rightarrow$ $HgCl_2(CNR)$

net wt gain by polymer : (0.66)(271.5) = 179.9 mg

(no wt loss)

$\therefore$ Amt Hg present = $\frac{0.66}{1.1799}$ = 0.56 mmol g^{-1}

$\therefore$ Amt Cl present = $\frac{(0.66)(2)}{1.1799}$ = 1.12 mmol g^{-1}

(e)For nickel:

Proposed reaction, assuming no oxidation:

$Ni(cod)_2 + CNR \rightarrow Ni(CNR) + 2\ cod$

Isocyanide content of polymer : 1.03 mmol g^{-1}

wt gain by polymer : (1.03)(274.7) = 282.9 mg

: (2)(1.03)(108) = 222.5 mg

net wt gain = 60.4 mg for 1 g of polymer

$\therefore$ Amt Ni present $= \frac{1.03}{1.0604} = 0.97$ mmol g^{-1}

(ii) Proposed reaction, assuming oxidation occurs:

$Ni(cod)_2 + CNR + O_2 \rightarrow 2\ cod + NiO(OCNR)$

wt gain by polymer : (1.03)(274.7) + (1.03)(32) = 315.9 mg

wt loss by polymer : (1.03)(108)(2) = 222.5 mg

net wt gain = 93.4 mg for 1 g of polymer

$\therefore$ Amt Ni present $= \frac{1.03}{1.0934} = 0.94$ mmol g^{-1}

Table 10

Isocyanide content of batches of resin used for the complexation reactions:

metal complex	isocyanide content of resin mmol g^{-1}
$RhCl_3.xH_2O$	0.56
K_2PtCl_4	0.90
Na_2PdCl_4	1.03
$AgNO_3$	1.03
$AgPF_6$	0.90
$FeCl_2$	1.03
$CoCl_2$	1.03
$HAuCl_4.3H_2O$	0.90
$CuCl_2.2H_2O$	1.03
$HgCl_2$	1.03
$[Rh(cod)Cl]_2$	1.03
$[Rh(CO)Cl]_2$	1.03
$Pt(cod)_2$	1.03
$Ni(cod)_2$	1.03
$Pd(dba)_2$	1.03

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